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Ministry of Education
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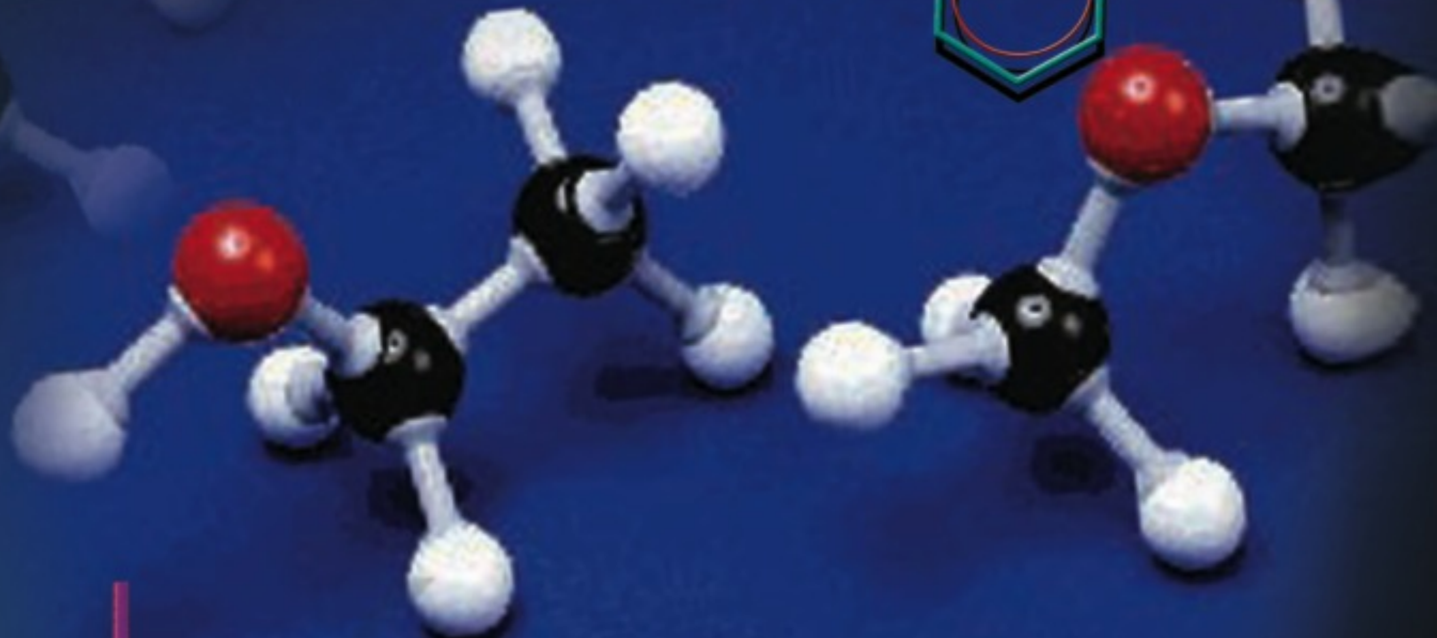
CHEMISTRY

For Third secondary



Titration

lithium ion battery

complementary colors

Effect of Heat on equilibrium

غير مصرح بتداول هذا الكتاب خارج وزارة التربية والتعليم

2016 - 2017

Arab Republic of Egypt
Ministry of Education
The Book Sector

CHEMISTRY

For

General Secondary Certificate

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غير مصرح بتداول هذا الكتاب خارج وزارة التربية والتعليم

المقدمة

في إطار تطوير التعليم لمواكبة المتغيرات العالمية و المحلية واستكمالا للجهود الحثيثة التي تقوم بها وزارة التربية و التعليم للارتقاء بمستوى المناهج الدراسية وربطها بالمجتمع والبيئة فقد كلف الأستاذ الدكتور وزير التربية والتعليم نخبة من أساتذة الجامعات المتخصصين بالتعاون والتنسيق مع موجهي الكيمياء بالوزارة وبمشاركة مؤلفي الكتاب السابق لإعادة تقييم ومراجعة المحتوى العلمي لمادة الكيمياء في المرحلة الثانوية .

ولقد قامت اللجنة المكلفة بإجراء التعديلات والإضافات اللازمة التي أدت إلى :

(1) التخلص من التكرار والحشو غير المبرر واستبعاد الأجزاء التي سبق للطالب دراستها وإعادة صياغة بعض أجزاء الكتاب بطريقة منطقية متسلسلة ومنظمة .
(2) إضافة بعض المفاهيم والتطبيقات لمواكبة الاتجاهات العلمية الحديثة.
(3) ربط موضوعات الدراسة بالحياة اليومية وتأثيراتها البيئية وتطبيقاتها الصناعية .
(4) الاهتمام بالمعالجات الرياضية في فهم بعض الموضوعات بهدف تقوية الجوانب الفكرية .
(5) إدخال بعض الموضوعات التي تتيح للطالب إجراء تجاربها معمليا لاكتساب مهارات عملية .
(6) إعداد بعض الإشكال التوضيحية وتوظيفها لخدمة المفاهيم العلمية.
(7) تحديد الأهداف المرجوة من دراسة كل فصل من فصول الكتاب وضعت في مقدمته لتعطى مؤشرا للطالب والمعلم على مدى ما حققه .
(8) تنوع التقييم ليتضمن قياس المستويات المختلفة للتعليم .

والكتاب في صورته الحالية يحتوى على خمس أبواب تتكامل وتترابط فيما بينها وتعكس تناغما مع محتويات كتب الكيمياء في المناهج العالمية وتشتمل على تطبيقات صناعية وبيئية مفيدة وتتضمن اهتماما واضحا بتنمية قدرات الفهم والابتكار وتتمشى مع المعايير القومية التي وضعتها الوزارة لتطوير منهج الكيمياء.

لجنة التطوير

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Chapter One

TRANSITION ELEMENTS

At the end of this chapter, the student must be able to:

- Recognize the elements of the first transition series.
- Recognize the economic importance the elements of the first transitionseries.
- Write the electron configuration of these elements.
- Explain why iron (II) ion is easily oxidized to iron(III) while manganese (II) ion is not easily oxidized.
- Determine the various oxidation stats of the elements.
- Define the transition element.
-Recognize the general properties of the transition elements.
- Explain the graduation in properties of the first transition series with the increasing in their atomic numbers.
- identifies the paramagnetic and the diamagnetic substance by using its electronic structure
- Clearfy the relation between the colors of the ions of transition elements and their electronic configuration.
- Explain reason for using elements of the first transition series as catalyst.
- Recognize the iron ores.
- Recognize the method of extraction of iron from its ores in the different furnaces .
- Recognize the alloys and their kinds .
-Enumerating the uses of alloys.
- Recognize the properties of iron and its oxides.

The transition elements:

We studded in the second year elements of (s) and (p) blocks which are found on both sides of the long form of periodic table, now we`ll study the transition elements which occupy the middle of the periodic table between (s) and (p) blocks.Including more than 60 elements

i.e. more than half the number of known elements.

These elements can be classified into:

1- Main transition elements.

2- Inner transition elements.

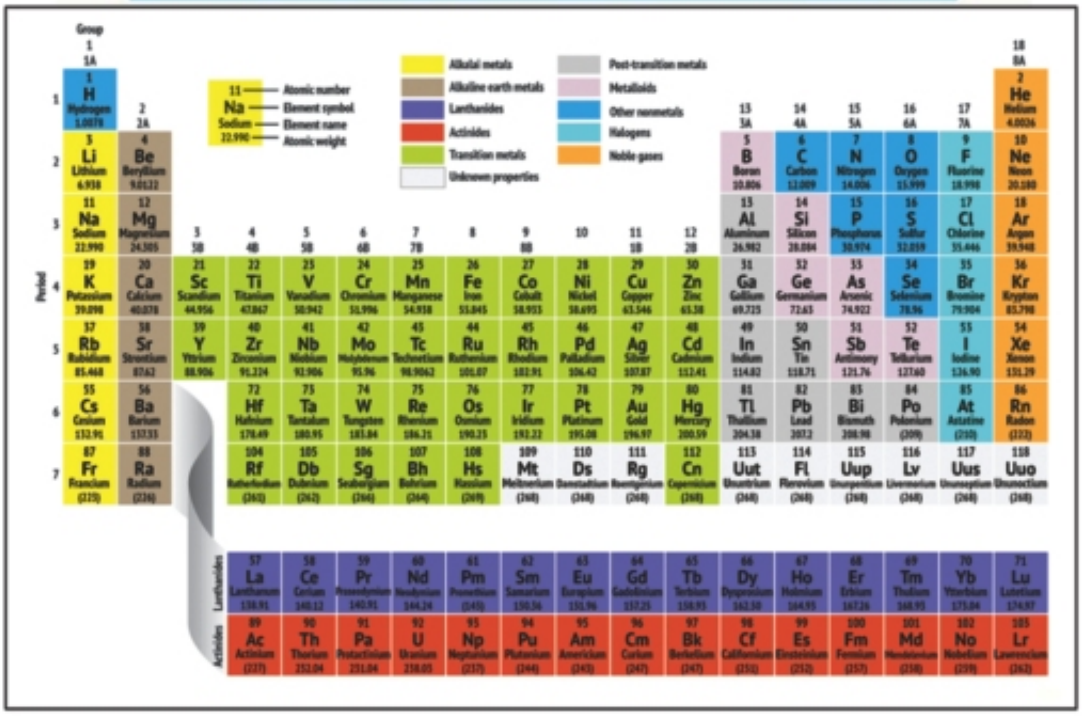
But we`ll study the main transition elements only:

The Main transition elements (elements of d- block):

In the main transition elements electrons occupying the d sublevel in sequence .Since the d-sublevel can take upto ten electrons, it contains ten vertical columns, These columns starts from the first column which contains all elements which are end with **nS^2 ,$(n-1)d^1$** to the last one which ends with **nS^2 ,$(n-1)d^{10}$** in which the d sublevel is filled in sequence.These columns from left to right of periodic table starts with the groups (3) IIIB, (4) IVB , (5)VB, (6)VIB , (7)VIIB and (8)VIII which contain three vertical column. (8),(9),(10) which are differing from the other transition elements of (B) in their properties, in which these elements are similar horizontally more the elements below in the same column.

These elements can be classified to four horizontal series which are:

Periodic Table of the Elements



I. The first transition series:

It includes the elements in which the sublevel (3d) is filled successively. They are found in the fourth periodafter calciumand consistsof ten elements startfrom scandium$_{21}$Sc ($4S^2,3d^1$) and ended with zinc $_{30}$Zn ($4S^23d^{10}$).

2. The second transition series:

It includes the elements in which the sublevel (4d) is filled successively. They are found in the fifth period and consist of ten elements start with yttrium$_{39}$Y ($5S^2,4d^1$) and ended withcadmium$_{48}$Cd ($5S^2,4d^{10}$).

3. The third transition series :

It includes the elements in which the sublevel (5d) is filled successively. They are found in the sixth period and consist of ten elements start with lanthanum$_{57}$La ($6S^2,5d^1$).and ended with Mercury$_{80}$Hg ($6S^2,4f^{14},5d^{10}$).

4. The fourth transition series :

It includes the elements in which the sublevel (6d) is filled successively.

They are found in seventh period..

1-The First Transition Series

This series contains ten elements which are scandium (Sc), titanium (Ti) vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn).

The following table represents the percent of each transition element in the earth's crust.

element	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn
% wt	0.0026	0.66	0.02	0.014	0.11	5.1	0.003	0.0089	0.0068	0.0078

All of these elements form nearly 7% of the weight ofearth's crust but they have high economic importance like:

1-Scandium

It is found in very small amount spread on a large area in the earth`s crust. On adding a little amount of scandium to aluminum it gives light and very hard alloy used in manufacture of Mig fighter jets also it is added to Mercury vapour lamps to produce light with high quality looks like sun light , so it is used in TV Photography at night.

2-Titanium

Strong element of rigidity as steel ,but it is less denser than steel, its alloys with Aluminum are used in the manufacture of aircraft and space shuttle because it maintains its durability at high temperatures while the hardness of aluminum decrease, it is used in the dental implants and artificial joints because, it is inert substance so the body does not eject it and does not cause any type of poisoning.from the famous Titanium compound Titanium dioxide (TiO_2) that is used in Sun protection cosmetics, where minute nanoparticles prevent effect of the UV on the skin. Titaniumis used in the dental implants

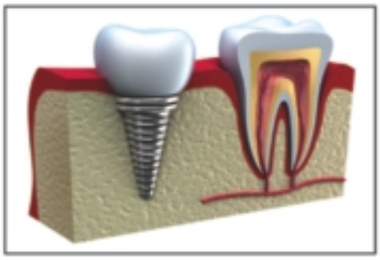


fig (1-2)

3-Vanadium

when we add a small portion of it to the steel, a high hardness alloy is formed and has great ability to resist corrosion so it is used in the manufacture of car springs.

From the important compounds of vanadium: Vanadium penta oxide is used in manufacture of dyes used in ceramics and glass industry; also it is used as a catalyst and manufacture of strong magnetic conductors.

4-Chromium

Itis chemically active metal but it resist the effect of the atmospheric air due to the formation of a larger metal oxide on its surface , in which themolecularvolume of the produced oxide is larger than that of the metal atoms which forms a nonporous layer of metal oxide that prevent the continued interaction with oxygen of air, Chromium is used in metal plating and leather tanning.

From the important compounds of chromium: Chromium III oxide Cr_2O_3 that used inmanufacture of dyes and potassium dichromate($K_2Cr_2O_7$) that used as oxidizing agent.

5-Manganese

Manganese is not usedas a pure metal because it is brittlemetal so always used as alloys or compounds. Ferromanganese alloy is used in railway track, because it is harder than steel, aluminum and manganese alloys are used in manufacture ofSoft drinks vessels (cans) because it resists corrosion.

The important compounds of manganese: Manganese dioxide MnO_2 which acts as strong oxidizing agent used in dry cell , potassium permanganate $KMnO_4$ that used as antiseptic substance and manganese II sulphate $MnSO_4$that used as a fungicide.

6-Iron

Used in manufacture of reinforced concrete, electricity pylons,knifes, gun and cannons pipes and surgical tools. Also used as a catalyst in the manufacture of ammonia by Haber-

Bosch method and the conversion of water gas (mixture of hydrogen and carbon monoxide) to a fuel by Fischer-Tropsch method.

7-Cobalt

It is similar to iron in which both of them can be magnetized so they are used in the manufacture of magnets. Cobalt is used in manufacture of modern dry batteries that used in cars.Cobalt has twelve radioactive isotopes, cobalt 60 is very important one because it produces gamma rays which have high penetrating power so it is used in food**preserving** processes, used for the detection of the quality of the industrial products, and to detects cracks and welding connections, and in **medicine** used for diagnosis and treatment tumors.

8- Nickel

It is used in the manufacture of nickel – cadmium battery which can be recharged. It forms with steel alloys which are hard and resist rust and the effect of acids. Nickel chromium alloys are used in heating coils and electric furnaces because they resist corrosion at high temperature, nickel is used for panting the other metals to protect them from oxidation and rust and give these metals beautiful appearance. Finally divided nickel is used as a catalyst like in hydrogenation processes of oil.

9-Copper

Copper is the first discovered metal, copper tin alloys are known as bronze alloy. Copper is good conductor of electricity so it is used in electric cables and coins industry, copper II sulphate $CuSO_4$is used as insecticide and fungicide in the purification of water. Fehling solution (one of copper compounds)is used to detect glucose in which its blue colour changes to orange.

10-Zinc

It is used in the galvanizing other metals to protect them from rusting.

From its compounds Zinc oxide ZnO is used in the manufacture of paints , rubber and cosmetics, zinc sulphide ZnS is used in manufacture of illuminating paints and x-ray screens.

The Electronic Configurations and Oxidation states:

The following table represents the electron configuration of the elements of the first transition series and their common oxidation states.(for illustration only)

The element	The group	The electron configuration	oxidation states	Some of the compounds
$_{21}Sc$	IIIB	$[Ar],4s^2,3d^1$	3	Sc_2O_3
$_{22}Ti$	IVB	$[Ar],4s^2,3d^2$	2 ,3 ,$\underline{4}$	TiO_2, Ti_2O_3, TiO
$_{23}V$	VB	$[Ar],4s^2,3d^3$	2, 3, 4, $\underline{5}$	V_2O_5 , VO_2 , V_2O_3 , VO
$_{24}Cr$	VIB	$[Ar],4s^1,3d^5$	2 ,$\underline{3}$,6	CrO_3 , Cr_2O_3 , CrO
$_{25}Mn$	VIIB	$[Ar],4s^2,3d^5$	2, 3, $\underline{4}$, 6, 7	MnO_2 , Mn_2O_3 , MnO $KMnO_4$, K_2MnO_4
$_{26}Fe$	VIII	$[Ar],4s^2,3d^6$	2 , $\underline{3}$, 6	Fe_2O_3 , FeO
$_{27}Co$	VIII	$[Ar],4s^2,3d^7$	2, $\underline{3}$, 4	, $CoCl_3$, $CoCl_2$
$_{28}Ni$	VIII	$[Ar],4s^2,3d^8$	$\underline{2}$, 3, 4	NiO_2 ,Ni_2O_3 ,NiO
$_{29}Cu$	IB	$[Ar],4s^1,3d^{10}$	1, $\underline{2}$	CuO ,Cu_2O
$_{30}Zn$	IIB	$[Ar],4s^2,3d^{10}$	2	ZnO

N.B. The oxidation state underline is the most stable one

1-The elements of the first transition series is located in the fourth period after calcium $_{20}Ca$ whoseits electronic configuration is [Ar] $4S^2$, After that there is a gradual filling of the five orbitals of (3d) sublevel by single electron in each orbital in sequence till manganese ($3d^5$). After manganese pairing of electrons takes place in each orbital till zinc ($3d^{10}$) (Hund's rule).

2-Chromium and copper are anomalous from the expected electronic configuration as their configurations are $_{24}Cr$ (Ar) $3d^5$ $4S^1$ and copper $_{29}Cu$ (Ar) $3d^{10}$ $4s^1$, in these elements

we find that their outer most sublevel 4s and 3d in chromium atom are half filled while in copper 4s is half filled but 3d is filled , this explain that the atom has low energy ,this means that it has extra stability when the outer most sublevel half filled(d^5) or filled (d^{10}) but this is not the only main factor that causes the stability of the atom.

Exercise:

Explain why iron (II) is easily oxidized to iron (III) whereas Mn (II) is not readily oxidized to Mn (III) ?

Solution : The electronic configuration of an iron atom is :$_{26}$**Fe:** $[Ar]3d^6 4s^2$

Fe^2 : [Ar] $3d^6$ Fe^{3+}: $[Ar]3d^5$

half-filled (d^5)more stable

Iron (III) ion is more stable as the 3d sublevel is half-filled $3d^5$ itismore stable so the reaction goes toward the formation of the more stable compound.

But in case of manganese atom the electronic configuration is $_{25}$Mn: $-[Ar]3d^5s^2$

Mn^{2+}:$3d^5$ Mn^{3+} :$3d^4$

half-filled (d^5) more stable

We find that the 3d sublevel is half-filled $3d^5$in Mn^{+2} ion so it is more stable than Mn (III) ion then Mn^{+2} ion is not readily oxidized to Mn^{+3} ion.

3-Allelements of the first transition series have oxidation state (+2) after losing the electrons of (4S) sublevel at first(except for scandium) .while in the higher oxidation states they lose the electrons of (3d) in sequence.

4- The oxidation states increase from scandium to manganese which has the highest oxidation state (+7) in group VIIB, after that the oxidation states decreases gradually to be (+2) in zinc in group IIB, from the previous we find that the maximum oxidation state not exceed its group number except for the group IB that contains copper, silver and gold.

5-The main transition elements are characterized by several oxidationstate (while in the representative metals have one oxidation state) this is can be explained as following when the atom of the main transition elements oxidized by losing electrons from 4s and 3d sublevels in sequence(which are close in energy) therefore the ionization potentials for the transition element increases gradually as its shown in ionization potential in kilo joule/ mole successive of oxidation states in vanadium.

$$\underset{4S^2,3d^3}{V} \xrightarrow[KJ/mol]{648} \underset{4S^1,3d^3}{V^{+}} \xrightarrow[KJ/mol]{1346} \underset{4S^o,3d^3}{V^{+2}} \xrightarrow[KJ/mol]{2858} \underset{4S^o,3d^2}{V^{+3}} \xrightarrow[KJ/mol]{4643} \underset{4S^o,3d^1}{V^{+4}} \xrightarrow[KJ/mol]{6523} \underset{4S^o,3d^o}{V^{+5}}$$

While in the representative metals like sodium, magnesium and aluminum , the increasing in the second ionization potential of sodium and the third of magnesium and the fourth of aluminum is very high due to breaking a complete energy level so it is difficult to obtain Na^{+2} or Mg^{+3} or Al^{+4} during the chemical reaction under normal conditions.

Application

$$\underset{(2S^2,2P^6,3S^2,3P^1)}{Al} \xrightarrow[KJ/mol]{578} \underset{(2S^2,2P^6,3S^2)}{Al^{+}} \xrightarrow[KJ/mol]{1811} \underset{(2S^2,2P^6,3S^1)}{Al^{+2}} \xrightarrow[KJ/mol]{2745} \underset{(2S^2,2P^6)}{Al^{+3}} \xrightarrow[KJ/mol]{11540} \underset{(2S^2,2P^5)}{Al^{+4}}$$

6- From the previous a general definition for the transition element can be obtained as follows:

The transition element

It is the element in which the orbitals of d or f occupied with electrons but not completely filledeither in its atomic state or in one of its oxidation states.

Exercise:1

Can coinage metals which are

$_{29}Cu$ ($3d^{10}$ $4s^1$), $_{47}Ag$ ($4d^{10}5s^1$) and $_{79}Au$ ($5d^{10}$ $6s^1$) be considered as transition elements?

<u>Solution :</u>

It is clear that the(**d**) sublevel is completely filled (**d^{10}**) in the three metals in the atomic state, but in the oxidation state (+2) or (+3) the sublevel (d) will be partially filled (d^9) or (d^8) , so they are transition elements..

Exercise:2

Are the metals zinc, cadmium and mercury be consider as transition elements?

$_{30}Zn$ ($4s^2$, $3d^{10}$) – $_{48}Cd$ ($5s^2$, $4d^{10}$) – $_{80}Hg$ ($6s^2$, $5d^{10}$)

It is clear that the(**d**) sublevel is completely filled (d^{10}) in the three metals in both atomic state and oxidation state (+2ion)

so they are not transition elements.

The general properties of the first transition elements

The following table shows some spatial datafor elements of this group which indicates their general properties by which this elements are characterized as following.

The element	The atomic mass	The atomic radius	The density g/cm^3	The melting point ^0C	The boiling point ^0C
Scandium Sc	45	1.44	3.10	1397	3900
Titanium Ti	47.9	1.32	4.42	1680	3130
Vanadium V	51	1.22	6.07	1710	3530
Chromium Cr	52	1.17	7.19	1890	2480
Manganese Mn	54.9	1.17	7.21	1247	2087
Iron Fe	55.9	1.16	7.87	1538	2800
Cobalt Co	58.9	1.16	8.70	1490	3520
Nickel Ni	58.7	1.15	8.90	1492	2800
Copper Cu	63.5	1.17	8.92	1083	2582

(the table for illustration only)

1- **<u>The atomic mass</u>:** It increases gradually with increasing their atomic number, but nickel is abnormal because it has five stable isotopes with average mass 58.7 u

2-Atomic radius:

Its noticed that there is a little change in atomic radii as we move through first transition series, Its also noticed that atomic radius is nearly constant from (Cr) to(Cu)

, this is due to two opposite factors:

a- The first factor causes decreasing in the atomic radius with increasing atomic number:

where The effective nuclear charge for these elements increases and also number of

electrons in the atom increases from (Sc) to (Cr) ,so the nuclear attraction to electrons increases which cause decrease the atomic radius.

b- The second factor causes increase the atomic radius:

The increasing in the number of the electron in 3d sublevel will increase the repulsion force between them.

As a result of these two opposite factors, atomic radii of these elements arerelatively constant .which explains using them in making alloys.

3- The Metallic property:

Appear clearly in these elements as following :

a-All of them are solid, having metallic luster and good conductivity of heat and electricity.

b-They have high melting and boiling points, due to the strong metallic bond which is formed due to the sharing of both 4s and 3delectrons in the formation of this bond.

c-most of them having high density which increases with the increasing in the atomic number ,because the atomic size is relatively constant with increase atomic mass.

d-There is variation in their activity of these elements - as copper has limited chemical activity, and some are moderate like iron that goes rusty if it exposed to air, and some are highly active like scandium which replaces hydrogen of water strongly.

4-The Magnetic properties :

There are two different magnetic properties which are

a- **Paramagnetic property**: which appear in the ions or atoms or molecules that have unpaired electrons in their orbitals (↑), which forms a magnetic field due to its spinning. Attracting external magnetic field.

The paramagnetic substance is known as the substance that attracts to the external magnetic field, due to the presence of unpaid electrons, the magnetic moment of the paramagnetic substances increases with the increasing in the number of the unpaired electrons.

(most of compounds of the transition elements are paramagnetic.)

b-Diamagnetic property

which appear in thesubstances having all orbitals are paired with electrons (↑↓ so their magnetic moment equal zero due to opposite spin motion of every pired electrons . Diamagnetic substance is the substance that repel the external magnetic field, due to Pairing of all its electrons

Exercise:

Which of the following substances is paramagnetic and which is diamagnetic?

Zn (d^{10}), Ni (II) ion (d^{8}), iron (II) chloride (d^{6}).

Write the order of the moment of these substances.

Answer :

Electronic configuration of (d) sublevel		number of unpaired electron electrons	Magnetic property
Zn (d^{10})	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0	diamagnetic
Ni^{2+}(d^{8})	↑↓ ↑↓ ↑↓ ↑ ↑	2	paramagnetic
Fe^{2+} (d^{6})	↑↓ ↑ ↑ ↑ ↑	4	paramagnetic

*The magnetic moments of the substance can be measured by the number of unpaired electrons.the measure of magnetic moments of the substance indicate the number of unpaired electrons and the electronic configuration of the metal ion:

Exercise:

Re arrange the following cations in ascending order according to their magnetic moment: $FeCl_3$,Cr_2O_3, TiO_2

5. Catalytic activity :

Transition elements are considered as ideal catalyst. Finally divided Nickel is used as catalyst like in the hydrogenation process and divided iron is used as a catalyst in the

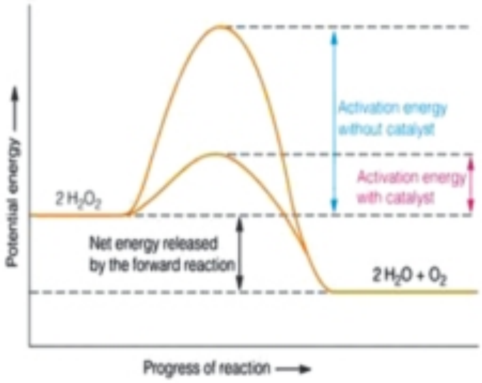
preparation of ammonia gas by Haber – Bosh method.

$$N_{2(g)} + 3H_{2(9)} \xrightarrow[Fe]{500^0C/200atm} 2NH_{3(9)}$$

Vanadium pent oxide $\mathbf{V_2O_5}$ is used as a catalyst during the preparation of sulphuric acid by the contact method.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[450^0C]{V_2O_5} 2SO_{3(9)}$$

$$SO_{3(s)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$



Effect of MnO_2 as a catalyst in decomposition of H_2O_2 . (fig 1-3)

The catalytic activity of the metals of the first transition series refers to presence of the 4S and 3d-electrons which can be used in the formation of bonds between the atoms of the surface of metal and the reacting molecules leading to the increase of concentration of these molecules on the surface of the catalyst weaken the bond in the reactant molecules and so decreases the activation energy which help to increase speed of reaction.

6. Coloured ions: Most of the compound of transition elements and their aqueous solutions are coloured, the following table show the colours of some hydrated ions of the metals of the first transition series.

(Table for illustration only)

No. of electrons in 3d of the ion	The colour		No. of electrons in 3d of the ion	The colour
$Sc^{+3}_{(aq)}$ ($3d^0$)	Colourless		$Fe^{+3}_{(aq)}$ ($3d^5$)	Yellow
$Ti^{+3}_{(aq)}$ ($3d^1$)	red violet		$Fe^{+2}_{(aq)}$ ($3d^6$)	Green
$V^{+3}_{(aq)}$ ($3d^2$)	Blue		$Co^{+2}_{(aq)}$ ($3d^7$)	Red
$Cr^{+3}_{(aq)}$ ($3d^3$)	Green		$Ni^{+2}_{(aq)}$ ($3d^8$)	Green
$Mn^{+3}_{(aq)}$ ($3d^4$)	Violet		$Cu^{+2}_{(aq)}$ ($3d^9$)	Blue
$Mn^{+2}_{(aq)}$ ($3d^5$)	Red (pink)		$Zn^{+2}_{(aq)}$ ($3d^{10}$)	colourless

Explanation the colour in materials:

The colour is formed due to the absorption of some photons in the area of visible light.Eye see only the remained colour (reflected) which is a mixture of some colours,

. if the substance absorb no light colour it appears white. If the substance absorb all visible light colour it appears black to eye

If the substance absorbs certain colour its colour appears by the complementary colour.

The following table shows the absorbed colour and its complementary (the reflected colour) .

Ex. Chromium (III) compounds absorb red colour so it appears green

The table and the shape show the pairs of complementary colour

Absorbed Colour	Complementary Colour
Violet V	Yellow Y
Blue B	Orange O
Green G	Red R
Yellow Y	Violet V
red R	Green G

(fig 1-4)

Complementary Colour

The relation between colours of transition elements ion and their electronic configuration:

From the above table we find that the hydrated ions of Sc^{+3} ($3d^0$) ,Zn^{+2} ($3d^{10}$) are colourless- also the nontransition elements contain orbitals of d empty (d^0) or completely filled (d^{10}). Then we can conclude that the colour in the transition elements ions is due to partially filling of the orbitals of **d** sublevel (1 – 9 electrons) i.e. due to the presence of the unpaired electrons in **d** sublevel.

IRON

$_{26}^{56}Fe : [Ar]\ 3d^6\ 4s^2$

Iron is the most important metal in heavy industries. Iron is the fourth most abundant element in the earth's crust after oxygen, silicon and aluminum as it forms(6.3%) of the earth's crust by mass and this mass increases gradually as we come close to earth core.

It is Found only in the form of pure metal (90%) in meteorites. Iron is found in the earth's crust in the form of natural ores which contains deferent iron oxides mixed with impurities.

The suitability of iron ore for extraction of iron based on:

The iron percentage in the ore, the composition of the impurities in the ore, and The type of harmful elements mixed with the ore such as sulphur, phosphorus ,arsenic and others.

The following table shows the most important iron ores :

The Ore	Chemical name	Chemical formula	Properties	Iron %	Place of deposits
1) Hematite	Iron III Oxide	Fe_2O_3	It has a blood red colour, it is more easily reduced	50-60	Oasis area (western desert)
2)Limonite	Hydrated ironIII oxide	$2Fe_2O_3.3H_2O$	Yellow hydrated oxide ,easily reduced	20-60	Oasis area
3) Magnetite	Magnetic iron oxide	Fe_3O_4	It is a black ore having magnetic properties	45-70	Eastern desert
4) Siderite	Iron II Carbonate	$FeCO_3$	It has a yellowish grey colour easily reduced	30-42	---

Extraction of Iron from its Ores

Firstly: Ore dressing:

Ore dressing process are carried out to realize the following :

1- Improving the physical and mechanical properties of iron ore, and includes

a- **Crushing processes**

The obtain the ore in suitable size to be easily reduced.

b- **Sintering processes:**

As a result of the crushing processes and cleaning furnace a huge amount of fine particles of ore are obtained which cannot be used directly in high furnace directly. These particles must be treated to collect them in larger size to be similar and homogeneous and this process is called sintering.

c-Concentrating processes :

This process is used to increase the percentage of iron by removes most of the impurities which are chemically combined or mixed with the ore, this is done by using the surface tension or magnetic or electric separation.

2- Improving the chemical properties:

Roasting :

In this process the ore is strongly heated in air for **:**

a) Drying the ore and expelling humidity, to increase the percentage of iron in the ore.

$$FeCO_{3(s)} \xrightarrow{\Delta} FeO_{(s)} + CO_{2(g)}$$

48.5% iron

$$2FeO_{(s)} + \frac{1}{2} O_{2(g)} \xrightarrow{\Delta} Fe_2O_{3(s)(69.6\%Fe)}$$

$$2Fe_2O_3 .3H_2O_{(s)(40\%Fe)} \xrightarrow{\Delta} 2Fe_2O_{3(s)(69.6\%Fe)} + 3H_2O_{(v)}$$

b) Oxidation of some impurities such as sulphur and phosphorus.

$$S_{(s)} + O_{2(g)} \xrightarrow{\Delta} SO_{2(g)}$$

$$4P_{(s)} + 5O_{2(g)} \xrightarrow{\Delta} 2P_2O_{5(g)}$$

Secondly : Reduction of Iron Ores :

In this stage the reduction of iron oxides to iron is carried out by one of two methods depending on the reducing agent:

a) Reduction, by carbon monoxide resulting from coke in the blast furnace.

$$C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$$

$$CO_{2(g)} + C_{(s)} \xrightarrow{\Delta} 2CO_{(g)}$$

$$3CO_{(g)} + Fe_2O_{3(s)} \xrightarrow{\Delta} 2Fe_{(s)} + 3CO_{2(g)}$$

b) Reduction by a mixture of carbon monoxide and hydrogen (water gas)resulting from natural gas (93% methane) in the midrex furnace.

$$2CH_{4(g)} + CO_{2(g)} + H_2O_{(v)} \xrightarrow{\Delta} 3CO_{(g)} + 5H_{2(g)}$$

$$2Fe_2O_{3(s)} + 3CO_{(g)} + 3H_{2(g)} \xrightarrow{\Delta} 4Fe_{(s)} + 3CO_{2(g)} + 3H_2O_{(V)}$$

Thirdly : Iron Production

After the reduction of iron ores in the blast furnace or Midrex furnace the third step in which the production of the different types of iron such as cast iron and steel.

Steel

The steel industry depends on two essential processes:

1. Removal of impurities from iron resulting from the furnaces.
2. Addition some elements to iron to produce steel with the required properties for industrial purposes.

The production of steel may formed by one of the following furnaces:

1. The Oxygen converters.2. Open-hearth Furnace.3. Electric Furnace.

ALLOYS

Alloys: are usually formed from two metals or more (such as the ferrochromium, ferromanganese, ferrovanadium, Ferronickel alloys)and it may consists of metal and other nonmetalsuch as carbon (steel).

Preparation of alloys:

1. By Melting: Alloys are usually prepared by melting the metals together and leavingthem to cool gradually.

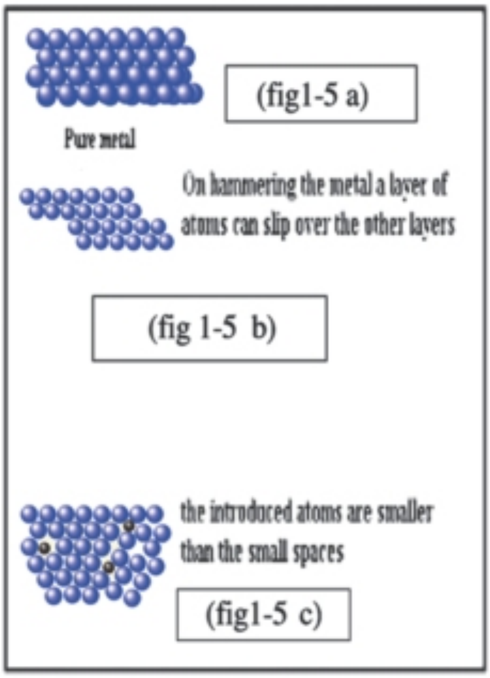
2.Byelectro deposition:

Alloys can also be obtained by electro deposition of two metals or more at the same time, such as electroplating .Iron handles with brass (Cu+Zn) by its deposition from a solution of copper and zinc ions.

Types of alloys:

1-Interstitial alloys:

Pure iron, as other metals, is formed of a Crystal lattice of metal atoms are arranged in compact closedrows.(fig 1-5 a)
On hammering, a layer of metal atoms Canslip one over the other. (fig 1-5 b)
Howeverthe introduce an element with small atomicsize to another pure metal in the Intermolecular spaces of the crystal lattice of the main element this prevent the movement of the metal layers (fig1-5 c) this will increase the hardness of the metal and change the physical properties of the metal like malleability , ductility ,melting point ,electric conductivity and magnetic properties ofmetal.Such as iron and carbon alloy (Steel).



(shape 1-5)

2-Substitutionalloys:

In this type of alloys some of the atoms of the pure metal are replaced by atoms of other metal which having the same atomic radius ,crystal lattice and the chemical properties such as(Ferrochrome alloy) in the stainless steel, (copper- gold alloy) and (ferronickel alloy).

3) Inter-metallic alloys:

In this type of alloys the elements forming the alloy combine with each otherchemically to form chemical compound.itschemical formula disobey valence law, and the compounds formed are solids consists of metals are not in the same group in the periodic table,

such as the two alloys (Aluminnm - Nikel) and (Aluminnm - Copper) that are called Duer alumin alloys.

And lead – gold alloy (Au_2Pb)and cementite (Fe_3C)

Properties of Iron

Pure Iron has no industrial importance because it is relatively soft,with low hardness , malleable ,ductile, withmagnetic properties, melts at 1538°C and its density is 7.87gm/cm^3. Its physical properties depend up on itspurity and the nature of its impurities. A large number of steels and other iron alloys may be produced with specific properties suitable for manyuses.

Chemical Properties:

Iron differs from the elements before it in the first transitionseries, where it has not the maximumoxidation state corresponding to the removal ofall electrons(8 electrons)from (4S and 3d).

- All the oxidation states above (+3) are not important.
- It has oxidation state (+2) which is correspondingto loss two electrons from (4s) sublevel ,

andoxidation state (+3) corresponding half-filled ($3d^5$) sublevel (stable state).

1. Effect of air :

Red hot iron reacts with dry air or oxygen producing magnetic iron oxide

$3Fe_{(s)} + 2O_{2(g} \xrightarrow{\Delta} Fe_3O_{4(s)}$

2. Effect of watervapour :

Red hot iron (500°C) reacts with water vapourproducing magnetic iron oxide and hydrogen gas.

$3Fe_{(s)} + 4H_2O_{(v)} \xrightarrow{500^0 C} Fe_3O_{4(s)} + 4H_{2(g)}$

3. with non-metals :

Iron reacts with chlorine producing iron (III) chloride and with sulphur producing iron (II) sulphide :

$2Fe_{(s)} + 3Cl_{2(g)} \xrightarrow{\Delta} 2FeCl_{3(s)}$

$Fe_{(s)} + S_{(s)} \xrightarrow{\Delta} FeS_{(s)}$

4. with Acids:

Iron dissolves in dilute mineral acids producing iron (II) salts not iron(III)salts which are reduced by product hydrogen.

$Fe_{(s)} + H_2SO_{4(aq)} \xrightarrow{(dil)} FeSO_{4(aq)} + H_{2(g)}$

$Fe_{(s)} + 2HCl_{(aq)} \xrightarrow{(dil)} FeCl_{2(aq)} + H_{2(g)}$

- Iron reacts with hot concentrated sulphuric acid producing iron (II) sulphate, iron (III) sulphate, sulphur dioxide and water :

$3Fe_{(s)} + 8H_2SO_{4(l)} \xrightarrow{(conc.)\ \Delta} FeSO_{4(aq)} + Fe_2(SO_4)_{3(aq)} + 4SO_{2(g)} + 8H_2O_{(v)}$

- Concentrated nitric acid cause passivity of iron due to the formation of a thin layer of oxide which protects the metal from further reaction. This layer can be removed by abrasion or by using dilute hydrochloric acid.

IRON Oxides

1-Iron (II) Oxide Fe O :

Preparation :

1. By heating iron (II) oxalate in absence of air

$$\begin{matrix} COO \\ | \\ COO \end{matrix}\!\!\!>\! Fe_{(s)} \xrightarrow[\text{in abcence of air}]{\Delta} FeO_{(s)} + CO_{(g)} + CO_{2(g)}$$

2. By reduction of higher oxides by hydrogen or carbon monoxide.

$$Fe_2O_{3(s)} + H_{2(g)} \xrightarrow{400\text{-}700^{\circ}C} 2\,FeO_{(s)} + H_2O_{(v)}$$

$$Fe_3O_{4(s)} + H_{2(g)} \xrightarrow{400\text{-}700^{\circ}C} 3\,FeO_{(s)} + H_2O_{(v)}$$

Properties :

1. It is black powder, insoluble in water.

2.Easily oxidized in hot air.

$$4\,FeO_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2\,Fe_2O_{3(s)}$$

3 . It reacts with mineral acids forming iron (II) salts and water.

$$FeO_{(s)} + H_2SO_{4(aq)} \xrightarrow{(dil.)} FeSO_{4(aq)} + H_2O_{(l)}$$

2- Iron (III)oxide Fe_2O_3:

Preparation:

1- On adding an alkali to an aqueous Solution of iron (III) salts ,

the(reddishbrown) iron (III)hydroxide precipitates.

.andheatingiron(III)hydroxide above 200^0C, it converts to iron (III) oxides.

$$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$$

(aq) (aq) (s) (aq)

$$2Fe(OH)_3 \xrightarrow[200^0c]{above} Fe_2O_3 + 3H_2O$$

(s) (s) (v)

2 . By heating iron (II) sulphate, iron (III) oxide is obtained:

$$2\,FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

(s) (s) (g) (g)

Its existence

This oxide present in nature in form of hematite

Properties:

1 - it is insoluble in water

2-It is used in red pigments in paints

2- It reacts with hot conc. mineral acids to form iron (III) salts and water.

Example

$$Fe_2O_3 + 3H_2SO_4 \xrightarrow[conc.]{\Delta} Fe_2(SO_4)_3 + 3H_2O$$

(s) (aq) (aq) (v)

<u>3- The black oxide (magnetic iron oxide) Fe_3O_4:</u>

Its existence

It can be conceder as a mixed iron (II) ,and iron (III)oxides knowing naturally as magnetite.

Preparation :

1.It is Prepared by the action of hot air or steam on red hot iron .

2. By reduction of iron (III) oxide .

$$\underset{(s)}{3Fe_2O_3} + \underset{(g)}{CO} \xrightarrow{230\text{-}300^{o}c} \underset{(s)}{2F_3O_4} + \underset{(g)}{CO_2}$$

Properties :

1- It strong magnet.

2- It reacts with hot concentrated acids to give iron (II) and iron (III) saltsproving that it is a mixed oxide:

$$\underset{(s)}{Fe_3O_4} + \underset{(l)}{4H_2SO_4} \xrightarrow[\Delta]{conc.} \underset{(aq)}{FeSO_4} + \underset{(aq)}{Fe_2(SO_4)_3} + \underset{(v)}{4H_2O}$$

3- It is oxidized to iron (III) oxide when its heated in air

$$\underset{(s)}{2Fe_3O_4} + \underset{(g)}{\frac{1}{2}O_2} \xrightarrow{\Delta} \underset{(s)}{3Fe_2O_3}$$

EVALUATION

QUESTION 1:-

Choose the correct answer:

1-The reaction of iron and sulphur gives …………

a-$Fe_2(SO_4)_3$ b-$FeSO_4$ c-Fe_2O_3 d-FeS

2-Iron dissolved in dil .acids giving……….

a-iron(II)salts b-iron(II)oxide c-iron(III) salt d-iron(III)oxide

3-Black iron oxide is a mixed oxide, it reacts with conc. hot acids giving ………..

a-iron(II)salts b-iron(III) salts c-(a and b) together d-iron (III) oxide

4-Reducing magnetic iron oxide at 400-700^{o} C gives…………

a-Fe b-FeO c-Fe_2O_3 d-$FeSO_4$

5-FeO reacts with dil. acids to give ………..

a-iron(II) salt only b-iron(III) salt only

b- iron(II) salt and water d-iron(III)salt and water

6-Heating iron (II)sulphate, produces iron (III)oxide ,sulphur dioxide and …..

a- hydrogen b-water c-sulphure trioxide d-hydrogen sulphide

7- Type of alloys in which the elements arebind together chemically is…..alloy

a-interstitial b- substitutional c-intermetallic d-(a and b)together

8- Chromium and iron forms ……….. alloy .

a- interstitial b-substitutional

c- intermetallic d- (a and c) together

QUESTION 2:-

Choose the electronic structure from column (B)of the element in column (A)and its use from column (C):

(A) Element	(B) Electronic Structure	(C) Uses
1-Titanium $_{22}Ti$	a-$[Ar]3d^{10},4s^{1}$	I- one from its compound is used as oxidizing agent and as antiseptics substance
2-Chromium $_{24}Cr$	b-$[Ar]\ 3d^{7},4s^{2}$	II- It is used in hydrogenation of oil.
3- Manganese $_{25}Mn$	c- $[Ar]\ 3d^{2}, 4s^{2}$	III-its isotope (60) is used in persevering food
4- Cobalt $_{27}Co$	d-$[Ar]3d^{8},4s^{2}$	IV- It is used in tanning leather
5- Nickel $_{28}Ni$	e-$[Ar]\ 3d^{5},4s^{1}$	V- its alloys used with aluminum in manufacture ofspace shuttle .
6- Copper $_{29}Cu$	f- $[Ar]\ 3d^{5},4s^{2}$	VI-it used for making Fehling solution .
		VII- manufacture of car springs

QUESTION 3:-

What happens if:

1- Heating iron (III) hydroxide over 200^{0}c .

2- Heating iron (II)sulphate strongly .

3- The reaction of haematite with conc. hot sulphuric acid.

4- Heating magnetic iron oxide strongly in air .

5- Heating iron (II)oxalate in absence of air .

6- Reduction of iron (III) oxide by hydrogen.

QUESTION 4:-

A'-Classify the following to diamagnetic or paramagnetic substances :

$CoCl_2$, $Fe_2(SO_4)_3$, $Zn\ SO_4$, $Fe\ Cl_2$

b- Classify the following to coloured or colourlesssubstances .

1- Iron (II) ion 2- Iron (III) ion

3-Titanium (III) ion 4-Scandium (III) ion

5-Copper (II) ion 6-Zinc(II) ion

QUESTION 5:-

Explain the role of each of the following :

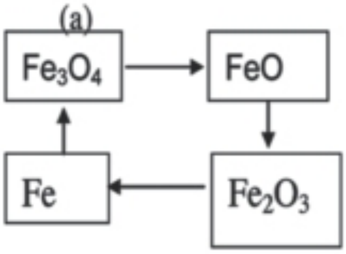
1-Coke in the blast furnace.

2- Natural gas in midrex furnace.

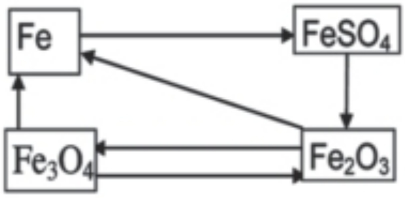
QUESTION 6:-

Write complete equations which express the reactions in the following diagrams.

(a)



(b)



QUESTION 7:-

Give reasons for :

1- The abnormal electronic configuration of both chromium and copper .

2- However chromium is a highly reactive element , it resists the effect of atmosphere .

3- Coinage metals (copper- silver- gold) are considered transition elements.

4- The decreasing in the atomic radius through the first transition series is not large.

5- Transition elements have high melting and boiling points

6- Most of transition elements attract to the external magnetic field.

7- Iron reacts with diluted acids to produce iron II salts not iron III salts.

8- Scandium doesn't produce Scandium Sc^{+4} ion.

9- Sc^{+3} and Zn^{+2} ions are colourless.

10- Iron III chloride is Para magnetic substance .

11- Concentrated nitric acid causes the passivity of iron.

12- Most of transition elements have catalytic activity.

CHAPTER TWO

Chemical analysis

Objectives

By the end of studying the chemical analysis chapter, student should be able to :

-remember the concepts and laws which have studded before and are related with other chapters

Explain the concept and types of chemical analysis.

- Identify the various quantitative qualitative analyses.

-Acquire the skill to identify some of acidic radicals

--Acquire the skill to identify some of basic radicals

- Identify the various quantitative volumetric analysis.

-Identify the various quantitative gravimetric analysis.

-Carry out an experiment for neutralization of a strong acid by strong base using a suitable indicator.

-compare between chemical indicators and their uses

-Acquire the accuracy skill for handling laboratory equipment.

-Appreciate the importance of studying the quantitative analysis for both the individuals and society.

-Formulate a positive attitude for the integration of mathematics and science together.

Feed Back

By revising the concepts and laws which you study before in the first and second secondary and has a relation with other chapters in the book.

*<u>Mole</u> : Quantity of substance which contains Avogadro's number of particles (Molecules or atoms or ions or formula units or electrons)

$$Al^{3+} + 3e^- \rightarrow Al$$

" 3 moles of electrons are needed to reduce 1 mole of Al^{3+} ions to form 1 mole of Al atoms"

*<u>Molar mass (g)</u> = The sum of atomic masses of the elements forming the molecule or formula unit measured in gram.

***Number of moles (mol)** = mass of substance (g) / Molar mass (g/mol)

***Number of molecules** (or atoms or ions) = number of moles of molecules x Avogadro's number (6.02×10^{23})

***volume of gas (L)** = number of molar gas (mol) x 22.4 (L/mol) at STP

* **Density of gas (g/L)** = molar mass (g/mol) / 22.4 (L/mol) at STP

***molar concentration** (M) = number of moles (mol) / volume of solution (L)

***the mass percentage of an element in compound (g/g%) =**

Mass of element in one mole of compound x100 / molar mass of the compound

***the mass percentage of compound in impure sample =**

Mass of compound in sample x100 / mass of impure sample

Chemical Analysis :

Chemical analysis is considered one of the important branches of chemical science which plays an important role in science progress, Also plays an important role in the progress of scientific fields such as , medicine, agricultural , food and environmental industries , etc....

In medical field :

diagnoses of diseases depends on chemical analysis to estimate the percentages of sugar , albumin , uremia ,and cholesterol and others , which makes it easier for the doctor in diagnoses and treatment , also estimating the amount of effective substances in medicines

In agricultural field :

Improving soil properties and crops depends on chemical analysis on the soil to know its properties concerning to acidity , basicity , kind and percent of elements present in it ,therefore it can be treated by adding the suitable fertilizers.

In Industrial field : Chemical analysis of ores and products is used in all industry fields , to determine its identity for standard specifications.

In Environmental field :

identify and measuring the harmful environmental pollutants content in water and foods , also percentages of carbon monoxide , sulphur dioxide , and nitrogen oxides gases in air, there are several examples that can't be counted that are based on chemical analysis that studies the chemical composition of substances.

Kind of chemical analysis :

if you have an analyzed substance which is need to identify its constituent elements ,percentage of each element and kind of bonding together to represent the molecular formula of matter or the group of compound if it's a mixture. and chemical analysis for substance takes place by two kind of analysis .

1-Qualitative analysis :

It involves the identification of the constituents of a substances wither it is pure (a sample salt) or mixture of several substances

2-Quantitative analysis:

It aims to estimate the percentage of each essential component of substance, accordingly practical qualitative chemical analysis should be done first to identify the component of compound in order to be able to choose the appropriate quantitative method to analyze them .

Firstly : Qualitative chemical analysis

We mentioned that qualitative analysis aims to know the component of substance whether it is pure substance or mixture of several substances,

if it is pure substance then it can be identified by their physical constants such as , melting point , boiling point , molar mass, etc…

If it is a mixture , firstly we must separate their component then identify them by the chemical method using suitable indicator .

So qualitative chemical analysis is considered as series of suitable chosen chemical reactions performed to detect the kind of main component for substance based on the changes occurring in the chemical reactions.

And qualitative chemical analysis includes...

a-The analysis of organic compounds :

it involves the identification of the elements and the functional groups composing the compound to identify it

b-the analysis of inorganic compounds:

it involves the identifications the ions which form the inorganic compound it include the identification of

-acid radical (anions) of salts

- basic radical (cations) of salts

in Qualitative analysis we will only study how to detect **cations** and **anions** for inorganic compound

A-detection for anions (Acidic radicals):

Anions can be classified into three groups, each group has a certain reagent , and these groups are :

1- Anions of dilute Hydrochloric acid group
2- Anions of Concentrated sulphuric acid group
3- Anions of Barium chloride solution group

(1) Anions of Dilute Hydrochloric acid group This group includes the following anions : carbonate $(CO_3)^{2-}$, bicarbonate $(HCO_3)^{1-}$, sulphite $(SO_3)^{2-}$, sulphide $(S)^{2-}$, thiosulphate $(S_2O_3)^{2-}$, nitrite $(NO_2)^{1-}$. this detection based on that Hydrochloric acid is more stable than the acids from which this anions are derived , ,when the acid react with salts of this anion , more stable acid replace less stable acid which easy to volatile or decompose to gases which we can detect them using suitable reagent where gently heating is preferred to eject gases

The following table illustrates the produced gases obtained from the reaction between hydrochloric acid and these anions.

1- Dilute Hydrochloric acid group

The main experiment: solid salt + Dilute Hydrochloric acid

Anion	Symbol	Gas liberated and Its detection	Confirmatory test for anion
(1) carbonate	$(CO_3)^{2-}$	$Na_2CO_{3(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$ Effervescence tacks place and CO_2 gas evolved which turn clear lime water milky $CO_{2(g)} + Ca(OH)_{2(aq)} \xrightarrow{S.T.} CaCO_{3(s)} + H_2O_{(l)}$	Salt solution + magnesium sulphate solution .a white ppt. is formed on cold soluble in hydrochloric acid. $Na_2CO_{3(aq)} + MgSO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + MgCO_{3(s)}$ $MgCO_{3(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

		CO_2 is passed for short time to avoid conversion of calcium carbonate to calcium bicarbonate so ppt. will disappear	**Note** all metal carbonates are water insoluble except sodium ,potassium and, ammonium carbonate and all carbonates are soluble in acids .
(2) Bicarbonate	$(HCO_3)^{1-}$	$NaHCO_{3(s)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$ Effervescence tacks place and CO_2 gas evolved which turn clear lime water milky **Note** all bicarbonates are soluble in water	Salt solution + magnesium sulphate solution . a white ppt. is formed after heat $2NaHCO_{3(aq)} + MgSO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + Mg(HCO_3)_{2(aq)}$ $Mg(HCO_3)_{2(aq)} \xrightarrow{\Delta} MgCO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$
(3) Sulphite	$(SO_3)^{2-}$	$Na_2SO_{3(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + SO_{2(g)}$ Sulphur dioxide gas evolved which has a very Irritating smell and turns a paper wet with potassium dichromate acidified by sulphuric acid to green	Salt solution + silver nitrate solution white ppt. is formed which turn black by heat $Na_2SO_{3(aq)} + 2AgNO_{3(aq)} \longrightarrow Ag_2SO_{3(s)} + 2NaNO_{3(aq)}$

		$K_2Cr_2O_{7(aq)} + 3SO_{2(g)} +$ $H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} +$ $Cr_2(SO_4)_{3(aq)} + H_2O_{(l)}$	
(4) Sulphide	S^{2-}	$Na_2S_{(s)} + 2HCl_{(aq)} \longrightarrow$ $2NaCl_{(aq)} + H_2S_{(g)}$ Hydrogen sulphide gas evolved which Has bade Smell, turns a paper wet with lead acetate to black $(CH_3COO)_2Pb_{(aq)} + H_2S_{(g)}$ $\longrightarrow PbS_{(s)} + 2CH_3COOH_{(aq)}$	Salt solution + silver nitrate solution black ppt. is formed from silver sulphide $Na_2S_{(aq)} + 2AgNO_{3(aq)}$ $\longrightarrow Ag_2S_{(s)} + 2NaNO_{3(aq)}$
(5) thiosulphate	$(S_2O_3)^{2-}$	$Na_2S_2O_{3(s)} + 2HCl_{(aq)} \longrightarrow$ $2NaCl_{(aq)} + H_2O_{(l)} + SO_{2(g)}$ $+ S_{(s)}$ Sulphur dioxide gas evolved and yellow ppt. as a result of suspend sulphur in solution	Salt solution + iodine solution $\longrightarrow$ the brown colour of iodine is removed $2Na_2S_2O_{3(aq)} + I_{2(aq)} \longrightarrow$ $Na_2S_4O_{6(aq)} + 2NaI$ (sodium Tetra thionate)
(6) Nitrite	$(NO_2)^-$	$NaNO_{2(s)} + HCl_{(aq)} \longrightarrow$ $NaCl_{(aq)} + HNO_{2(aq)}$ $3HNO_{2(aq)} \longrightarrow HNO_{3(aq)}$ $+ H_2O_{(l)} + 2NO_{(g)}$	Salt solution + potassium permanganate acidified by conc. sulphuric acid The violet colour of permanganate is removed

		Colourless nitric oxide gas evolved which turned reddish brown at the mouth of the tube $2NO_{(g)} + O_2 \longrightarrow 2NO_{2(g)}$	$5NaNO_{2(aq)} + 2KMnO_{4(aq)} + 3H_2SO_{4(aq)} \longrightarrow 5NaNO_{3(aq)} + K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 3H_2O_{(l)}$

(2) Concentrated sulphuric acid group

This group includes the following anions:

Chloride (Cl^-) , bromide (Br^-) , Iodide (I^-) , and nitrate $(NO_3)^-$

This detection is based on that concentrated sulphuric acid is more stable than the acid from which these anions are derived. on adding Concentrated hot sulphuric acid

To the salts of these anions it displaces these acids which appear in the form of gases and can be detected by suitable reagent

The main experiment:

Add concentrated sulphuric acid to the solid salt and heat if necessary.

Anions	Gas liberated	Confirmatory tests
Chloride (Cl^-)	HCl gas is evolved , which is colourless . it gives white fumes with glass rod wet with ammonia solution . $2\ NaCl_{(s)} + H_2SO_{4\,(L)} \xrightarrow{conc./\Delta} Na_2SO_{4(aq)} + 2HCl_{(g)}$ $HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$	Salt solution + silver nitrate solution white ppt. is formed from silver chloride which turns violet in sun light , soluble in conc. ammonia solution $NaCl_{(aq)} + AgNO_{3(aq)} \longrightarrow AgCl_{(s)} + 2NaNO_{3(aq)}$

Bromide (Br^-)	HBr gas is evolved , which is colourless . it partially oxidized by sulphuric acid and orange red fumes from bromine will be separated turns a paper wet by starch yellow. $2NaBr_{(s)} + H_2SO_{4\,(l)} \xrightarrow{conc./\Delta}$ $Na_2SO_{4(aq)} + 2HBr_{(g)}$ $2HBr_{(g)} + H_2SO_{4\,(l)} \rightarrow 2H_2O_{(l)} + SO_{2(g)} +$ $Br_{2(v)}$	Salt solution + silver nitrate solution white-yellow ppt. is formed from silver bromide which turns dark in sun light , soluble slowly in conc. ammonia $NaBr_{(aq)} + AgNO_{3(aq)} \longrightarrow$ $AgBr_{(s)} + NaNO_{3(aq)}$
Iodide (I^-)	HI gas is evolved , which is colourless . it partially oxidized quickly by sulphuric acid and violet fumes from iodine will be separated after heat turns a paper wet by starch blue. $2KI_{(s)} + H_2SO_{4\,(l)} \xrightarrow{conc./\Delta}$ $K_2SO_{4(aq)} + 2HI_{(g)}$ $2HI_{(g)} + H_2SO_{4\,(l)} \xrightarrow{conc.} 2H_2O_{(l)} + SO_{2(g)}$ $+ I_{2(v)}$	Salt solution + silver nitrate solution yellow ppt. is formed from silver iodide insoluble in ammonia solution $NaI_{(aq)} + AgNO_{3(aq)} \longrightarrow$ $AgI_{(s)} + NaNO_{3(aq)}$
Nitrate ($(NO_3)^-$)	Brown vapour of nitrogen dioxide evolves due to the decomposition of the HNO_3 The density of vapour increased by	**<u>The brown ring test .</u>** Nitrate salt solution + freshly prepared solution of iron II sulphate + few drops of conc. H_2SO_4 are carefully added on

	adding copper felling $2NaNO_{3(s)} + H_2SO_{4(l)} \xrightarrow{conc./\Delta}$ $Na_2SO_{4(aq)} + 2HNO_{3(l)}$ $4HNO_{3(l)} \xrightarrow{\Delta} 2H_2O_{(l)}$ $+ 4NO_{2(g)} + O_{2(g)}$ $4HNO_{3(l)} + Cu \xrightarrow{conc./\Delta} Cu(NO_3)_{2(aq)} +$ $2H_2O_{(l)} + 2NO_{2(g)}$	inner surface of tube. A brown ring appears at the interface Of acid and reactant solutions Disappears by heat or shaking $2NaNO_{3(aq)} + 6FeSO_{4(aq)} +$ $4H_2SO_{4(l)} \xrightarrow{conc} Na_2SO_{4(aq)}$ $+ 3Fe_2(SO_4)_{3(aq)} + 4H_2O_{(l)} +$ $2NO_{(g)}$ $FeSO_{4(aq)} + NO_{(g)} \longrightarrow$ $FeSO_4.NO_{(s)}$ brown ring compound

Barium chloride solution group

This group includes the anions of phosphates $(PO_4)^{3-}$, and sulphate $(SO_4)^{2-}$

This test is based on the fact that the anions of this group do not react with dil HCl or conc. H_2SO_4 but they give ppt. when react with barium chloride solution.

(1) **Phosphates** $(PO_4)^{3-}$	Salt solution + barium chloride solution → a white ppt. of barium phosphate soluble in Dil HCl $2Na_3PO_{4(aq)} + 3BaCl_{2(aq)} \longrightarrow$ $Ba_3(PO_4)_{2(s)} + 6NaCl_{(aq)}$	Salt solution + silver nitrate solution yellow ppt. is formed from silver phosphate soluble in both ammonia solution and nitric acid $Na_3PO_{4(aq)} + 3AgNO_{3(aq)}$ $\longrightarrow Ag_3PO_{4(s)} + 3NaNO_{3(aq)}$
(2) **sulphate**	Salt solution + barium chloride	Salt solution + lead (II)acetate

$(SO_4)^{2-}$	solution → a white ppt. of barium sulphate insoluble in Dil HCl $Na_2SO_{4(aq)} + BaCl_{2\,(aq)} \rightarrow BaSO_{4\,(s)} + 2NaCl_{\,(aq)}$	solution →a white ppt. of Lead(II) Sulphate $Na_2SO_{4(aq)} + (CH_3COO)_2Pb_{(aq)} \rightarrow 2CH_3COONa_{\,(aq)} + PbSO_{4(s)}$

B- Identification of basic radical

Identification of basic radical is more complicated than that of acidic radicals due to the presence of a great number of basic radicals also in their interference each other . also the same radical may have more than one oxidation state

basic radicas are divided into six analytical groups. and each group has its reagent which is called group reagent .

classification depend on fiffering in solubility of thesalts of these metals in water

for example metal chloride of the first analytical group which are chloride of silver(I) , mercury (I) , lead (II) are sparingly soluble in water so they can be precipitated as chloride on adding the group reaget which is dil hydrochloric acid

we well study some examples of the six analytical groups

<u>second analytical group:</u>

cations of this group are precipitated in the form of sulphides in acidic medium , by dissolving the salt in water and adding dilute Hydrochloric acid to it to make solution acidic then passing hydrogen sulphide gas to it.Cu^{2+} is one from this group

<u>Test for copper (II) cation Cu^{2+}</u>

Copper (II) salt solution + group reagent ($HCl + H_2S$) black ppt. from copper(II)sulphide is formed soluble in hot nitric acid

$CuSO_{4(aq)} + H_2S_{(g)} \rightarrow H_2SO_{4(aq)} + CuS_{\,(s)}$

third analytical group:

they are precipitated as hydroxides using ammonium hydroxide if they are not mixed with other cations .

cations to be studied: aluminium , iron(II) , iron(III)

The main experiment: salt solution + ammonium hydroxide (group reagent)

Cation	Reaction with group reagent	Confirmatory test
Aluminium Al^{3+}	$Al_2(SO_4)_{3\,(aq)} + 6NH_4OH_{(aq)} \rightarrow 3(NH_4)_2SO_{4(aq)} + 2Al(OH)_{3(s)}$ White gelatinous ppt. of Aluminium hydroxide soluble In dil. Acids and in caustic soda	Salt solution + sodium hydroxide solution White gelatinous ppt. of Aluminium hydroxide soluble in excess sodium hydroxide forming sodium meta aluminate $Al_2(SO_4)_{3\,(aq)} + 6NaOH_{(aq)} \rightarrow 3Na_2SO_{4(aq)} + 2Al(OH)_{3(s)}$ $Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow NaAlO_{2\,(aq)} + 2H_2O_{(l)}$
Iron (II) Fe^{2+}	$FeSO_{4\,(aq)} + 2NH_4OH_{(aq)} \rightarrow (NH_4)_2SO_{4(aq)} + Fe(OH)_{2(s)}$ White ppt. turns white green When it exposed to air and soluble in acids	Salt solution + sodium hydroxide solution White green ppt. of iron(II)hydroxide is formed $FeSO_{4\,(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + Fe(OH)_{2(s)}$

Iron (III) Fe^{3+}	$FeCl_3 + 3NH_4OH_{(aq)} \rightarrow$ $3NH_4Cl + Fe(OH)_{3(s)}$ Reddish brown gelatinous ppt. Soluble in acids	Salt solution + sodium hydroxide solution Reddish brown ppt. of iron(III)hydroxide is formed $FeCl_{3\,(aq)} + 3NaOH_{(aq)} \rightarrow$ $3\,NaCl_{(aq)} + Fe(OH)_{3(s)}$

Fifth Analytical group

Cations of this group are precipitated as carbonates by addition of ammonium carbonate .

We study calcium ion as an example for this group.

The main experiment: salt solution + ammonium carbonate solution (group reagent)

Cation	Reaction with group reagent	Confirmatory tests
Calcium Ca^{2+}	$CaCl_{2(aq)} + (NH_4)_2CO_{3(aq)} \rightarrow$ $2NH_4Cl_{(aq)} + CaCO_{3(S)}$ a white ppt. of calcium carbonate soluble in dil. HCl and also in water contaening CO_2 $CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \rightarrow$ $Ca(HCO_3)_{2(aq)}$	1) Salt solution + dil. Sulphuric acid A white ppt. of calcium sulphate Is formed $CaCl_{2(aq)} + H_2SO_{4(aq)} \rightarrow$ $2HCl_{(aq)} + CaSO_{4(s)}$ 2) flame test: Volatile calcium cation gives bunsen flam a brick red colour

Secondly Quantitative analysis

1-Volumetric Analysis

This method is based on measurement of the volumes of the substance to be analyzed. It is based upon measuring the amount of a reagent of known concentration (standard solution) which added to known volume of substance to find its conc. that is completely consumed by the analyze . measuring conc. Of acid or base using base or acid knowing their conc. And volume This process is known as (titration) .

To select the standard solution, the suitable reaction which will take place between the solutions of two substances should be known.

These reactions may be :

1. Neutralization reactions which are used for determination of acids and bases.
2. Oxidation – reduction reactions which are used for determination of redox substances.
3. Precipitation reactions which are used for determination of substances that form sparingly soluble products in water .

If the analyze is an acid, a standard solution of an alkali or base (sodium hydroxide or sodium carbonate) may be used for titration. If the analyte has some basic character, a standard acid solution is used for titration and so on.

To detect the point at which complete reaction takes place **(end point),**

Its point at which neutralization reaction between acid and base is completed.

Some indicators which change their colours in the reaction medium are used to detect the end point of reaction.

The following table shows some indicators used in the neutralization reactions (Figure 1-2)

Indicator	Colour in acidic medium	Colour in basic medium	Colour in neutral medium
Methyl orange	Red	Yellow	Orange
Phenolphthalein	Colourless	Red	colourless
Litmus	Red	Blue	purple
Bromothymol blue	Yellow	Blue	pale green

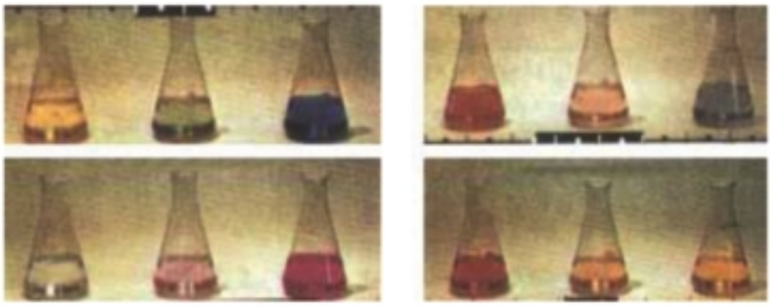


Fig :2-1

Fig :2-2

This can be illustrated in the determination of sodium hydroxide solution of unknown concentration with a standard 0.1 molar hydrochloric acid . A 25 ml of the alkali solution is transferred to a conical flask using a pipette followed by two drops of a suitable indicator solution (Methyl orange or Phenolphthalein) A burets is filled up with standard hydrochloric acid solution.

The acid is added gradually to the alkali solution (Figure 2-2) in small quantities until the alkali has been neutralized completely as shown by the change in the colour of the indicator.

The reaction is represented by the following equation:

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

If the volume of the acid added from the burette till the end of the reaction is 21 ml , therefore:

The number of moles of added acid

$$= \frac{\text{volume} \times \text{concentration}}{1000} = \frac{21 \times 0.1}{1000} = 2.1 \times 10^{-3} \text{moles}$$

This means that the number of moles of sodium hydroxide present in 25 ml of the solution $= 2.1 \times 10^{-3}$

Number of moles in one liter $= \frac{2.1 \times 10^{-3} \times 1000}{25} = 0.084$ moles / L

Therefore , the concentration of sodium hydroxide solution =0.084 moles/liter . You can simplify the calculation by substituting in the following mathematical equation:

$$\frac{M_a V_a}{n_a} = \frac{M_b V_b}{n_b}$$

Where : M_a=concentration of the acid used (mole/liter).

V_a=volume of acid used (ml).

n_a= number of moles of the acid shown in the chemical equation.

M_b=concentration of the alkali used(mole / liter).

V_b= volume of the alkali used (ml).

n_b=number of moles of alkali shown in the chemical equation.

In the above example:

Hydrochloric acid Sodium hydroxide

$$\frac{M_a V_a}{n_a} = \frac{M_b V_b}{n_b}$$

$$\frac{0.1 \times 21}{1} = \frac{M_b \times 25}{1}$$

Concentration of the alkali $(M_2)=\frac{1\times21\times0.1}{25\times1}=0.084$ moles/liter

Example(1):

A 20 ml of calcium hydroxide solution [$Ca(OH)_2$] was titrated with 0.05 molar hydrochloric acid . At the end of reaction , 25ml of the acid was consumed . Calculate the concentration of calcium hydroxide (mole/liter) .

Solution:

$$2HCl_{(aq)} + Ca(OH)_{2\,(aq)} \rightarrow CaCl_2 + H2O_{(l)}$$

Hydrochloric acid   Calcium hydroxide

$$\frac{Ma\ Va}{n_a} = \frac{Mb\ Vb}{n_b}$$

$$\frac{0.5\times25}{2} = \frac{Mb\times20}{1}$$

Concentration of calcium hydroxide $(M_b)=\frac{1\times0.5\times25}{2\times20}=0.0312$ moles/liter

Example (2):

A 0.1gram of a mixture of solid substance containing sodium hydroxide and sodium chloride was titrated with 0.1 molar hydrochloric acid .The complete reaction (end point) takes place by the consumption of 10 ml of the acid .Calculation the% sodium hydroxide in the mixture.

Solution:

Number of moles of of hydrochloric acid used $=\frac{10\times0.1}{1000}=0.001$ mole

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H2O_{(l)}$$

1 mol   1 mol   1 mol   1mol

From the balanced equation

It is known that 1 mole of sodium hydroxide reacts with 1 mole of hydrochloric acid, therefore the concentration of sodium hydroxide=0.001 mole/liter

1 mole of sodium hydroxide = 40 grams

The mass of sodium hydroxide in the mixture = $40 \times 0.001 = 0.04$ grams

% Sodium hydroxide in the mixture $= \frac{0.04 \times}{0.1} 100 = 40\%$

2-Gravimetri Analysis

This method depends on the separation and determination of the mass of the analyte and by using chemical calculation ,the quantity of analyte can be measured .

Two approaches are used for analyte separation:

(A)Volatilization method

(B) Precipitation Method

(A)Volatilization method

This method is based on the volatilization of the element or compound to be determined followed by its measurement either by collecting the volatile material and determining its mass or by measuring the amount lost from the original mass of the substance.

Example:

A 2.6903 grams of hydrated barium chloride salt ($BaCl_2 . xH_2O$) was strongly heated until a constant mass of 2.2923 grams . Calculate the % of water of crystallization of the hydrated barium chloride . Find out the number of water molecules of crystallization and write the molecular formula of the salt . (O=16 , H=1 , Cl =35.5, Ba=137).

Solution:

Mass of water of crystallization=2.6903-2.2923=0.398 grams

This mean that2.2923grams of anhydrous barium chloride combined with 0.398 grams of water of crystallization .

$\therefore$ % Water of crystallization $= \dfrac{0.398}{2.6903} \times 100 = 14.79\,\%$

$\because$ The molecular formula of $BaCl_2$ equals a mass of (137+71)=208 grams combined with (x) gram of water of crystallization ,

$\therefore$ X mass of water of crystallization in the molecular formula

$= \dfrac{208 \times 0.398}{2.2923} = 36.114$ grams

$\because$ Molecular mass of water =(1×2)+(16×1)=18 grams

$\therefore$ The number of molecules of water of crystallization $= \dfrac{36.114}{18} = 2.006$ molecules

$\therefore$ The molecular formula of hydrated barium chloride is $BaCl_2.2H_2O$.

(B) Precipitation Method

This method is based on precipitation of the analyte in the form of pure sparingly soluble compound with constant and known chemical structure. The precipitate is isolated from the solution by filtration on an ash less filter paper (a type of filter papers upon ignition leaves no ash). The filter paper with the precipitate is transferred to an ignition crucible and completely ignited until volatilization of the constituents of the filter paper. The mass of the precipitate remains after ignition ,is weighed and used for determining the mass of the analyte .An example is the precipitation of barium in the form of barium sulphate

Example:

Sodium sulphate solution was added to a solution of barium chloride till complete precipitation of barium sulphate . The mass of the isolated precipitate after filtration and drying was found to be 2 grams. Calculate the mass of barium chloride in the solution. (O=16, S=32, Cl=35.5, Ba=137)

Solution:

Write a balanced equation and calculate the molecular masses of the substances in relation . In this case there are barium chloride and barium sulphate .

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$

1mol

$208 \text{ grams} \rightarrow 233 \text{ grams}$

$X \text{ grams} \rightarrow 2 \text{ grams}$

$$X(\text{mass of barium chloride}) = \frac{208 \times 2}{233} = 1.785 \quad \text{grams}$$

Evaluation

Question 1:-

Explain by balanced chemical equation How can you differentiate practically by experiment between each pair of the following salts :

a- Sodium sulphite , Sodium sulphate

b- Iron II chloride , Iron III chloride

c- Sodium nitrite , Sodium nitrate

d- Sodium chloride , aluminum chloride

Question 2 :-

Write the name and formula of acidic or basic radicals which gives the following product during test them

a- Salt solution + sodium hydroxide solution produce white green ppt.

b- Salt solution + magnesium sulphate solution produce white ppt. after heat

c- Salt solution + silver nitrate solution produce yellow ppt. insoluble in ammonia solution

Question 3 :-

Write one use for the following reagent with explanation by symbolic equation:

a- Ammonium hydroxide

b- Barium chloride

c- Silver nitrate

d- Acidified Potassium permanganate

Question 4 :-

Choose the right answer from those below each sentence:

a- Salt solution + barium chloride solution produce white ppt. insoluble in acids

a- Nitrate b- phosphate c- sulphate d- nitrite

b- Salt solution + lead(II) acetate solution produce black ppt.

a- Sulphate b- Nitrate c- phosphate d- sulphide

c- Salt solution + sodium hydroxide solution produce reddish brown ppt.

a- Copper(II) b- iron(III) c- aluminum d- iron(II)

d- Solid salt + hydrochloric acid produce gas has irritating smell with yellow ppt.

a- Sulphide b- carbonate c- thiosulphate d- sulphite

Question 5:-

Give reason for with explanation by symbolic equation whenever possible

a- On adding sodium hydroxide gradually to aluminum chloride solution white ppt. is produced then disappear

b- Dilute hydrochloric acid is not used to differentiate between salts of sodium carbonate and bicarbonate.

c- The violet colour of potassium permanganate solution acidified by sulphuric acid Will be removed by adding potassium nitrite solution.

d- Filter paper wetted by lead (II) acetate solution turns black when it exposit to hydrogen sulphide gas.

e- violet vapour will produced during reaction between conc. sulphuric acid and potassium iodide with heat

Question 6:-

Choose from column (A) what is suitable from column (B) :on adding silver nitrate solution to the solution of the some anions , a ppt. is formed

(A)	(B)
1- soluble in ammonia solution	Phosphate
2- soluble slowly in ammania solution	Bromide
3- insoluble in ammonia solution	Chloride
4- soluble in nitricacid and ammonia solution	Sulphide

Question 7:-

Sodium hydroxide solution is added to three salt solutions of chlorides, the following are formed :

First white gelatinous ppt.

Second reddish brown ppt.

Third white green ppt.

Mention the basic radical for every one of the three salts, and write the equations of the reactions

Question 8:-

Hydrochloric acid is added to three sodium salts in solid stat

First gas evolved which has a very Irritating smell and turns a paper wet with Acidified potassium dichromate to green

Second Colourless gas evolved which turned reddish brown at the mouth of the tube

Third Colourless gas evolved which has Irritating smell with suspension of yellow substance.

Mention the acidic radical for every one of the three salts, and write the equations of the reactions

Question 9:-

A 25 ml of sodium hydroxide solution was titrated with 0.1molar sulphuric acid solution . The acid volume consumed at the equivalent point is 8 ml, calculate the concentration of sodium hydroxide solution .

Question 10:-

Calculate the volume of 0.1 molar hydrochloric acid solution required for titration Of 20 ml of 0.5 molar sodium carbonate solution till complete reaction

Question 11:-

Find out the mass of sodium hydroxide present in 25 ml solution which consumes , by titration ,15 ml of 0.1 molar hydrochloric acid solution .

Question 12:-

A 2 gram of impure sodium chloride was dissolved in water. Excess of silver nitrate was added to precipitate 4.628 grams of silver chloride .Calculate the % of chlorine in the sample.

Chapter three

Chemical Equilibrium

Objectives

By the end of studying the chemical equilibrium unit, students should be able to:

- Identify the equilibrium system.
- Illustrate the factors affecting the rate of chemical reaction
- Write the statement of the law of mass action .
- Apply the law of mass action on balanced reactions and calculate the equilibrium constant.
- Numerate the factors affecting the state of equilibrium
- Write the statement of Le Chatelier's principle
- Carry out some calculations related to the chemical equilibrium.
- Clarify the concept of ionic equilibrium.
- Explain the ionization of water and ionic product of water.
- Clarify the concept of pH and its significant on aqueous solutions .
- Explain the concept of hydrolysis.
- Clarify the concept of solubility product and its applications.
- Appreciate the high accuracy of universe creation by God .
- Appreciate the efforts of scientists, for the development of chemistry.

Chemical Equilibrium

The equilibrium systemis apparently a stationary system but in reality dynamic. If water in a closed vessel is heated, we notice happening two opposite processes. These are evaporation and condensation processes . At the beginning of heating, rate of evaporation is predominates which followed by an increase in the vapour pressure (vapour pressure is the pressure due to water vapour in air at a certain temperature).

The evaporation process continues until the vapour pressure equals saturated water vapour pressure (which is the maximum water vapour pressure in air at a certain temperature).

Eventually a state of equilibrium is reached between the rate of evaporation and rate of condensation. At this time the number of water molecules which evaporate is equal to the number of water vapour molecules condense

$$\text{Water (liquid)} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{water (vapour)}$$

Similar to the equilibrium established in physical systems, equilibrium in many chemical reactions takes place and the chemical reactions can be divided into two types :

1. Complete (irreversible) reactions.
2. Reversible reactions.

(1) <u>Complete reactions</u>

In this type the reactions goes mostly in one direction (approximately forward). Where it is difficult for the produced material which contains gas or precipitate to combine together again to form reactant material under the same reaction condition.

Examples for complete reaction

A. On addition of sodium chloride solution to a silver nitrate solution ,notes that ' a white precipitate of silver chloride is formed.

$$NaCl_{(aq)} + AgNO_{3(aq)} \longrightarrow NaNO_{3(aq)} + AgCl_{(s)}$$

B- When a strip of magnesium metal is placed in hydrochloric acid solution, hydrogen gas evolved.

$$Mg_{(s)} + 2HCl_{(l)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$

(2) Reversible reactions

During reaction between one mole of acetic acid with one mole of ethyl alcohol , it is expected according to the following equation , that one mole of ester (ethyl acetate) and one mole of water should be formed.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

Acetic acid ethyl alcohol Ethyl acetate ester water

On testing the reaction solution using blue litmus paper, it turns red, in spite of the produced materials having neutral effect on litmus.

What is the reason for the observed acidity?.

The previous reaction does not complete reaction which proceed in one direction , towards the formation the products only, it considered as a reversible reaction , which proceed in both directions; forward and backward.

Forward direction :-

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \longrightarrow CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

Backward direction :-

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

Accordingly, both the reactants and products are always found in the reaction medium at equilibrium . This explains the acidity of reaction mixture due to the presence of acetic acid .

Chemical equilibrium in reversible reactions :

It is a dynamic system takes place when the rate of forward reaction equals the rate of backward reaction , and The concentrations of the reactants and products are not changed : The equilibrium position remains unchanged since all reactants and products are still found in the medium of reaction , (no gas evolves , no precipitate is formed) and as long as the reaction conditions such as temperature and pressure are not changed .

Rate of chemical reaction

The rate of a chemical reaction is measured by change in concentration of the reactants per unit time. The concentration unit is expressed as mole / liter from solution and the time unit is expressed as second or minute. During the complete chemical reaction , the concentration of the reactants decreases till nearly consumed and the concentration of the products increases (Figure 3-2) , but in case of reversible reactions ,the increase in the concentration of the products and decrease in the concentration of the reactants proceed until an equilibrium state is established (Figure 3-1) .

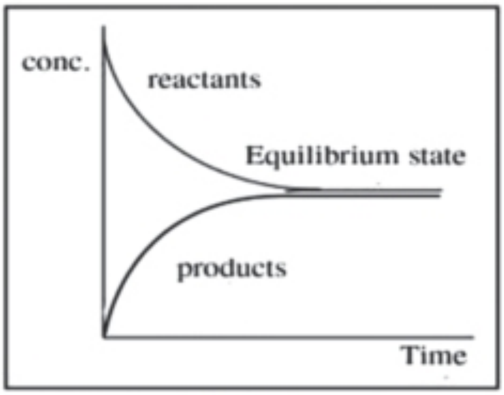


Fig :3-1

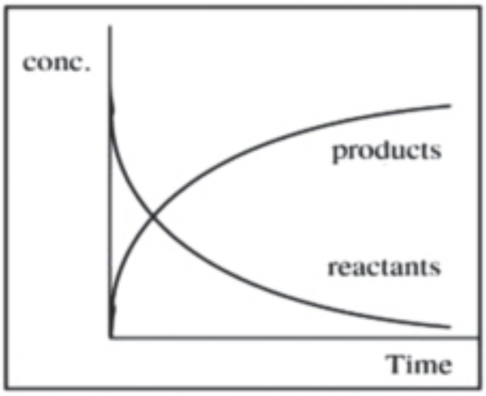


Fig :3-2

And from the chemical reactions that are relatively ending in a very short time. They are almost instantaneous reactions such as the reaction of silver nitrate with sodium chloride to form a springly soluble precipitatate of silver chloride as soon as the reactants are mixed .

Other reactions are comparatively slow such as the reaction between plants oil and caustic soda to form soap and glycerol. Some reactions such as iron rusting are even need several months to takes place.

Factors affecting the rate (speed) of chemical reactions :-

The rate of chemical reactions is affected by several factors, these are:

1-Nature of the reactants . 2- Concentration of the reactants.

3- Reaction temperature. 4- Pressure.

5- Catalysts. 6- Light.

1- Nature of the reactants :- This includes two important factors :-

A-Type of bonding in the reactants:-

Ionic reactants undergo very fast reactions instantaneously as in the case of the reaction between sodium chloride and silver nitrate. Ions of the reactants combine with each other as soon as their solutions are mixed .

On the other hand, covalent bonded reactants undergo slow reactions as in the case of organic reactions .

B-Surface area exposed to the reaction :-

The surface area exposed to the reaction plays an important role in the rate of the reaction. For example when two equal masses of zinc metal ; one in the form of powder , the other in the form of a block , are placed, each separately, in a test tube ,and an equal volume of dilute hydrochloric acid is added to each , you can observe that the reaction with zinc powder is completed in shorter time than that with zinc block.

So with increase surface area of reactant exposed to the reaction rate of reaction increase.

2- Concentration of reactants:-

With increase number of the reacting molecules (i.e. with increasing concentration), the chance of collision increase and the speed of reaction increase. The Norwegian scientists **Waage** and **Guldberg** established a law expressing the relationship between velocity of the chemical reaction and concentration of the reactants. This law is known as the law of mass action

Law of mass action: - At a constant temperature, the rate of a chemical reaction is directly proportional to the result of multiplication of the reactant concentrations; each is raised to the power of the number of molecules or ions in the balanced chemical equation.

This law explain the effect of concentration on rate of reaction.

To clarify the law of mass action , you can perform the following experiment : by gradual addition of iron (III) chloride solution (pale yellow colour) to ammonium thiocyanate solution (colourless) ,the colour of the reaction mixture becomes blood red due to the formation of iron (III) thiocyanate, The reaction can be represented by the following equilibrium :

$$FeCl_3(aq) + 3NH_4SCN(aq) \rightleftharpoons Fe(SCN)_3(aq) + 3NH_4Cl(aq)$$

$FeCl_3(aq)$ +	$3NH_4SCN(aq)$	⇌	$Fe(SCN)_3$ (aq) + $3NH_4Cl(aq)$
ironIIIchloride	ammonium thiocyanate		ironIII thiocyanate
(pale yellow)	(colourless)		(blood red)

If an excess amount of iron (III) chloride is added, the red colour of the solution increases indicating formation of more iron(III) thiocyanate.

When the rate of the backward reaction (r_2) equals the forward reaction (r_1), in the above reaction an equilibrium state is established and both reaction rates are expressed as follows:

$r_1 \alpha [FeCl_3] [NH_4SCN]^3$

$r_1 = k_1[FeCl_3] [NH_4SCN]^3$

$r_2 \alpha [Fe(SCN)_3] [NH_4Cl]^3$

$r_2 = k_2 [Fe(SCN)_3] [NH_4Cl]^3$

The square brackets [ ] represent the concentration in unit (mole / liter) whereas k_1 and k_2 are rate constants for the forward and backward reactions ,respectively.

<u>At equilibrium:</u> $r_1 = r_2$

$k_1 [FeCl_3][NH_4SCN]^3 = k_2[Fe(SCN)_3][NH_4Cl]^3$

$$\frac{k_1}{k_2} = K_c = \frac{[Fe(SCN)_3] \quad [NH_4Cl]^3}{[FeCl_3] \quad [NH_4SCN]^3}$$

The product of $\frac{K_1}{K_2}$ is a constant value referred to as K_c and is known as the equilibrium constant of the reaction:

Example:-

Calculate the equilibrium constant of the reaction :

$$I_{2(g)} + H_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Provided that the concentrations of I_2 ,H_2 and HI at equilibrium are 0.221 , 0.221 and 1.563 mole/liter , respectively .

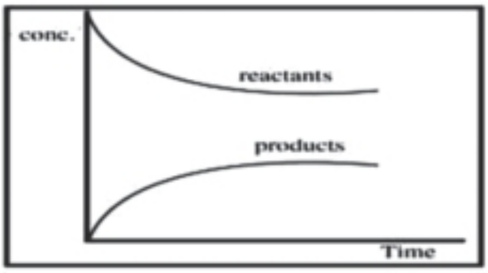


Fig :3-3

Solution :-

$$Kc = \frac{[HI]^2}{[H_2] \quad [I_2]}$$

$$= \frac{(1.563)^2}{0.221 x 0.221} = 50$$

It should be noticed that :

(a) The small values of equilibrium constant (Kc<1) mean that the result of multiplication of the product concentrations (nominator) is less than the result of multiplication of the reactant concentrations (denominator) each is raised to the power of the number of moles, which reveal that the reaction is not proceed well towards the formation of the products and that the reversed reaction has an effective role . (fig 3-3)

As an example is the solubility of silver chloride in water .

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \quad , \quad Kc = 1.7 \times 10^{-10}$$

Value of Kc in above reaction indicate that silver chloride is sparingly soluble in water

(b) The high values of equilibrium constant(K_C>1) indicate that the reaction proceeds almost to its end .This means that the forward reaction is the predominant reaction, as in the case of the reaction of chlorine with hydrogen .

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \qquad K_c = 4.4 \times 10^{32}$$

(c) The concentration of pure water as solvent, solid substances and precipitates should not appear in the equilibrium constant equation, because their concentrations remain generally constant whatever their quantities, as their values don't significantly change .

(d) At same temperature value of equilibrium constant does not change by change the concentration. Of reactants or products.

3- Effect of temperature on the rate of reaction :-

The effect of temperature on the rate of chemical reaction can be explained by collision theory . This theory assumes that: to have a chemical reaction, molecules of the reactants must collide with each other. Only molecules of very high speed can react, since their kinetic energy is high enough to break the bonds within the molecules so that the chemical reaction can take place. Therefore the

molecule must have a minimum amount of kinetic energy to react during collision. This minimum amount of energy is known as the “activation energy”

Activation energy is defined as: The minimum amount of energy that must be gained by a molecule to react at collision.

Activated molecules: Are those molecules which have kinetic energy that equals or exceeds the activation energy.

We can deduce from this theory , that a raise in temperature causes an increase in the proportion of activated molecules and consequently an increase in the rate of chemical reaction .The rate of many chemical reactions is doubled by increasing the reaction temperature 10° C .

Experiment to illustrate the effect of temperature on a reaction at equilibrium:

If we bring a flask filled with nitrogen dioxide gas (reddish brown colour) and placed it in a cooling mixture, we observe that the intensity of the colour decreases gradually, until this reddish brown colour disappeared (Figure3-4).

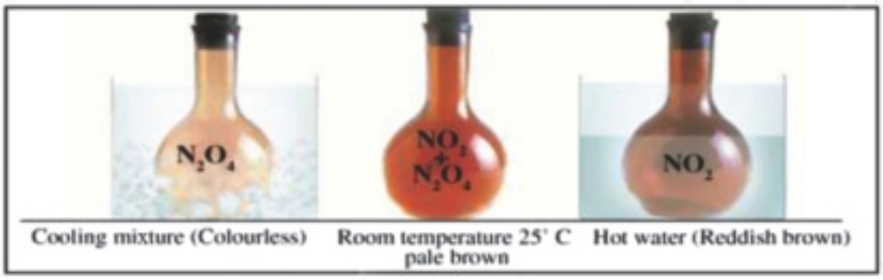


Fig :3-4

When the flask containing the gas is removed from this cooling mixture and kept at room temperature (25° C), we found that the reddish brown colour starts to reappear gradually, until returns back to first state, the colour degree increases as temperature rises up.This can be explained according to the following equilibrium equation .

$$2NO_{2(g)} \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} N_2O_{4(g)} + \text{heat}$$

(Reddish brown) (colourless)

We deduce from last experiment that if an exothermic reaction has reached the equilibrium state , decrease in temperature force the reaction to proceed in the forward direction in order to liberate heat.

4- Effect of pressure :

It is worth mentioning that the concentration of a substance in the solution is given in a terms of molarity and is expressed by placing the substance between two square brackets [ ] . If the reactants or products are in the gaseous state , the concentration is expressed by using their partial pressure. For example , ammonia gas is prepared in industry from its elements according to the following reaction:

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\text{high pressure/cooling}} 2NH_{3(g)} \quad , \Delta H = -92Kj$$

4 moles are react to form 2 moles from ammonia molecule, i.e., the formation of ammonia gas is followed by a decrease in the number of moles and consequently a reduction in the volume. It was found that by applying pressure and cooling, the rate of ammonia formation increases.We can conclude from the above example that by increasing the pressure or cooling on a gaseous reaction under equilibrium, a shift in the direction of reducing the volume (or the direction in which volume is less) takes place.

In this case, the equilibrium constant is expressed by the symbol Kp to indicate that the concentrations of the substances are expressed by the partial pressure:

$$Kp = \frac{(P_{NH3})^2}{(P_{N2}) \text{ X } (P_{H2})^3}$$

As in Kc the value of Kp for the reaction does not change by change partial pressure of reactant or product gases at same temperature and the total pressure

of reaction is the summation of all partial pressure of gases (and depend on the number of moles for each gas)

Example: Calculate the equilibrium constant (Kp) of the reaction:

$$N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

Provided that the pressures are NO_2= 2 atm, O_2=1 atm and N_2=0,2 atm.

Solution:

$$Kp = \frac{(P_{NO_2})^2}{(P_{N_2}) \times (P_{O_2})^2} = \frac{(2)^2}{0.2 \times 1^2} = 20$$

$\therefore$ The equilibrium constant =20

From the above observations and others , Le Chatelier ,a French scientist , formulated a rule named after his name . This rule predicts the effect of different factors such as concentration, temperature and pressure on the systems under equilibrium.

Le Chatelier's principle :

The changes in any conditions of a system under equilibrium such as concentration , pressure or temperature the system activated to direction which decrease or cancels the effect of change.

(5) Effect of catalysts :

We have seen that slow reactions proceed at a faster rate by heating. But in industry this is very expensive , resulting in an increase of the cost of products due to the additional cost of the fuel used for heating . Chemists have found that slow reactions can be accelerated by using certain substances which increase the reaction rate without raising the temperature

These substances are called catalysts.

Catalysts are known as" ***substances that little amount from it cause a change in the rate of chemical reaction without itself being change or change equilibrium position".***

Catalysts decrease activation energy of reaction and increase rate of reaction in both forward and backward at same time

Catalysts are used in more than 90% of the industrial processes such as food and petrochemical industries. Catalysts are also used in catalytic converters utilized in cars to convert the gaseous combustion products, which cause air pollution, into safe products. Catalysts are metals, metal oxides or compounds.

Enzymes (are protein molecules produced in the living cells) act as catalysts in many biological and industrial processes.

(6) Effect of light :

Some chemical reactions are affected by light , the photosynthesis is an example in which chlorophyll in plants absorbs light and form carbohydrates in the presence of carbon dioxide and water.

Photographic films contain silver bromide in a gelatinous layer .When light falls on it , positive silver ions accept electrons from negative bromide ions and are converted to silver metal . Bromine is absorbed in the gelatinous layer.

The increase in light intensity is associated with an increase in the amount of silver formed .

$$Ag^{+} + e^{-} \rightarrow Ag$$

IONIC EQUILIBRIUM

Applications of the law of mass action in ionic equilibrium :

1. Electrolyte Solutions:

There are solid materials like sodium chloride ionized completely into positive and negative ions when they dissolve in water and their solutions are good conductors of electricity. These materials are known as ionic compounds whose "+ve" and "-ve" ions are bonded by electrostatic attraction forces.

The covalent compounds, the bonds between their atoms are polar covalent bonds such as hydrogen chloride gas and pure acetic acid, which are ionized in the presence of water, Hydrogen chloride gas is ionized approximately 100% while the ionization of .acetic acid is very limited This can be verified by the following experiments:

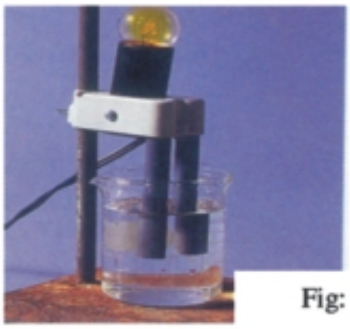
Experiment. (1) :

Test the electrical conductivity of pure (glacial) acetic acid, and hydrogen chloride gas dissolved in benzene, using the apparatus shown in Figure (3-5). You notice that the lamp doesn't illuminate in both cases, this indicate that the two solutions don't contain ions that conduct the electric current.

Experiment. (2) :

Dissolve 0.1 mole of hydrogen chloride gas in 1L of water, and 0.1 mole of pure acetic acid in 1L of water to obtain two acidic solutions of equal concentration of hydrochloric acid and acetic acid. Test elelectric conductivity of these solutions.You notice that the lamp illuminates strong in the case of hydrochloric acid and gives faint light in the case of acetic acid as shown in Fig(3-5) , this indicate that the first solution contains excess of ions than the other solution.

HCl in water **Acetic acid in water**



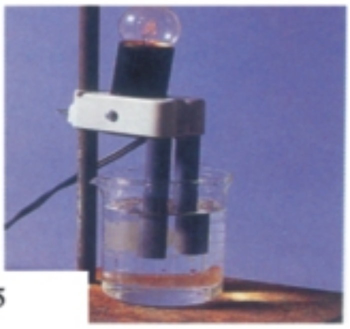


Fig: 3-5

<u>Experiment. (3) :</u>

Test for the effect of dilution of the previous solutions, on their electric conductivity (the strength of illumination of the lamp) during the dilution of 0.01 mol/L-0.001mol/L and notice what happens. You notice the illumination doesn't change by the dilution of hydrochloric acid but it increases by the dilution of acetic acid.

<u>Conclusion:</u>

From all the previous experiments we can deduce that:

Covalent compounds such as dry hydrogen chloride and pure acetic acid ionize in water . Ionization of hydrogen chloride is complete ionization, but acetic acid is very limited. This is the reason of the good conductivity of the first acidic solution for electricity and the bad conductivity of the second acidic solution. So the ionization of hydrochloric acid is not affected by dilution while the ionization of acetica acid increases by dilution that indicates that there are unionized molecules in the solution.

According to the previous observations the ionization of these acids can be represented as follows:

$$HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

The following table represents the ionization constants of some weak acids: (for illustration only)

Acid	Chemical formula	Ionization constant (k_a)
Sulphurous acid	H_2SO_3	1.7×10^{-2}
Hydrofluoric acid	HF	6.7×10^{-4}
Nitrous acid	HNO_2	5.1×10^{-4}
Acetic acid	CH_3COOH	1.8×10^{-5}
Carbonic acid	H_2CO_3	4.4×10^{-7}
Boric acid	H_3BO_3	5.8×10^{-10}

Hydroxonium ion:(hydronium ion)

There is no free hydrogen ion (proton) produced from the ionization of acids in their aqueous solution, because it attracts to the lone pair of electrons in oxygen atom of the water molecule and combines with water molecule by a co-ordinate bond. This proton is called hydrated proton or hydronium ion $[H_3O]^+$.

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

We can summarize the previous concepts as follows:

Ionization: a process in which unionized molecules are changed into ions.

Complete Ionization: a process in which all unionized molecules are changed into ions, and this happens in strong electrolytes.

Incomplete (weak) Ionization: a process in which a small part of unionized molecules are changed into ion, and this happens in weak electrolytes. In which two opposite processes are always found in the solution, which are dissociation of molecules into ions and combination between the ions to give molecules. An equilibrium state arising between the ions and the unionized molecules. This can be represented by the following equation :

$$\underset{\text{Weak electrolyte}}{AB} \rightleftharpoons \underset{\text{free ions}}{A^{+} + B^{-}}$$

This type of equilibrium is known as **ionic equilibrium**.

Ionic equilibrium:-

It is the equilibrium arising between molecules of a weak electrolyte and the ions resulting from it.

The law of mass action can not be applied in the case of strong electrolytic solution because they are completly ionized.

Ostwald (1988) discovered the relation between the degree of ionization - alpha (α) and concentration (C) mol / L for the solutions of weak electrolytes.

Ostwald law :-

Suppose that we have one mole of A weak monoprotic acid (HA) dissociates in water according to the equation :

$$\underset{\text{Weak electrolyte}}{HA} \rightleftharpoons \underset{\text{free ions}}{H^{+} + A^{-}}$$

By applying the law of mass action on this equilibrium system, the following relation is obtained:

$$Ka=\frac{[H^{+}][A^{-}]}{[HA]}$$

$[H^+]$,$[A^-]$ and [HA] represent the concentrations of the ions produced and the unionized molecules acid at the equilibrium state K_a. which is the equilibrium constant of ionization. When one mole of a weak acid (HA) dissolves in (V) liter of the solution , then at equilibrium :

$$\text{Degree of dissociation} = \frac{\text{Number of dissociated moles}}{\text{Total number of moles before dissociation}}$$

If the number of dissociated moles is (α) mole then, the number of Unionized moles from HA= (1-α) and the number of moles of (H^+)and (A^-) produced equals α mole.

$\because$ The concentration (C) = $\frac{\text{Number of moles}}{\text{Volume by liter (V)}}$

$\therefore$ The concentration of the substance (mole/ liter) at equilibrium is

$$\underset{\text{Weak electrolyte}}{HA} \rightleftharpoons \underset{\text{free ions}}{H^+ + A^-}$$

$$\frac{(1-\alpha)}{V} \quad = \quad \frac{\alpha}{v} \quad \frac{\alpha}{v}$$

Substitution in the equation of mass action gives :

$$K_a = \frac{[\frac{\alpha}{v}][\frac{\alpha}{v}]}{[\frac{1-\alpha}{v}]} = \frac{\alpha^2}{v(1-\alpha)}$$

This relation is known as Ostwald's Law for dilution which represents the quantitative relationship between the degree of ionization (α) and dilution .

It can be seen that :

At a constant temperature, the degree of ionization (α) increases by dilution (K_a remains constant) . In case of weak electrolytes, the degree of ionization (α) is small and can be neglected. Where the value (1-α) is considered approximately one and the relation becomes :

$$K_a = \frac{\alpha^2}{V}$$

Since the concentration of the weak acid (c_a) = $\frac{1}{V}$ mole /liter .

The previous equation becomes:

$$K_a = \alpha^2 \times C_a$$

$$\therefore \alpha = \sqrt{\frac{K_a}{C_a}}$$

This means that increasing dilution (decreasing concentration) causes an increase in dissociation degree and vice versa .

Example : Calculate the degree of dissociation in 0.1 molar hydrocyanic acid (HCN) solution at 25°C , providing that the equilibrium constant of the acid K_a= $7.2x10^{-10}$

Solution :

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$

Applying Ostwald Law : $K_a = \alpha^2 \text{ x } C$

$$7.2 \text{ x } 10^{-10} = \alpha^2 \text{ x } 0.1$$

$$\therefore \alpha^2 = \frac{7.2x10^{-10}}{0.1} = 72x10^{-10}$$

$$\alpha = \sqrt{72 \text{ x } 10^{-10}} = 8.5 \text{ x } 10^{-5}$$

Calculation of hydronium ion concentration of weak acids :

When a weak acid such as acetic acid with a concentration (C_a) dissociates in water according to the equation :

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH3COO^-_{(aq)} + H_3O^+_{(aq)}$$

The dissociation constant for such reaction

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

From the above equation , the quantity of acetate ion (CH_3COO^-) released equals the quantity of hydronium ion (H_3O^+) produced:

$[H_3O^+] = [CH_3COO^-]$

$\therefore$ The equilibrium constant is :

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

Since the acid is weak , the amount dissociated (α) is small and can be neglected. So, the concentration of acetic acid at equilibrium (C_a -α) equals the original acetic acid concentration (C_a) Consequently:

$$K_a = \frac{[H_3O^+]^2}{C_a} \qquad \therefore [H_3O^+] = \sqrt{C_a x\, K_a}$$

Example :

Calculate the hydrogen ion concentration in 0.1 molar acetic acid solution at 25°C , provided that the equilibrium constant of the acid is 1.8×10^{-5} .

Solution :

$$[H_3O^+] = \sqrt{C_a x\, K_a}$$

$$[H_3O^+] = \sqrt{1.8 \times 10^{-5} x\, 0.1} = 1.342 \times 10^{-3} \text{ molar}$$

Calculation of the hydroxyl ion of weak bases :

Partially ionized bases in aqueous solutions are known as weak bases. The concentration of hydroxyl ion can be calculated the same method , that used for hydronium ion . For example, when ammonia, a weak base , is dissolved in water the following equilibrium reaction takes place :

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

This equation reveals that one mole of both NH_4^+ and OH^- ions is formed.

$$K_b = \frac{[OH^-]^2}{[NH_3]}$$

Since the dissociation constant of ammonia is small, a small portion of ammonia dissociates and at equilibrium, the concentration of the remaining ammonia $[NH_3]$ equals the original concentration of ammonia = (C_b)

$$K_b = \frac{[OH^-]^2}{C_b} \text{ , } [OH^-] = \sqrt{C_b x K_b}$$

2. Ionization of water:

Pure water is a very poor conductor of electricity, but some conductivity is detected, so some ionization of water must take place as shown in the following equation :

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

To simplify, this equation can be written:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant is expressed by the relation:

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14}$$

From the value of the equilibrium constant, it is clear that a very small number of water molecules ionized.

The number of unionized water molecules can be considered as a constant value.

Therefore, the above relation can be rewritten as follows;

$$K_w = [H^+][OH^-] = 10^{-14}$$

Since water is neutral to litmus, the concentration of H^+ that responsible for the acidic properties equals the concentration of OH^- that responsible for the basic properties. Then

$$K_w = [10^{-7}][10^{-7}] = 10^{-14}$$

K_w(ionic product of water):

The result of multiplication of the concentration of hydrogen ion [H^+] and hydroxide ion [OH^-] that produced from the ionization is definef as the ionic product of water that equals $1X10^{-14}$. which is a constant value.

If the concentration of hydrogen ion increases, the concentration of hydroxyl ion decreases with the same amount . So, if the concentration of one of these ions is known, the concentration of the other can be deduced.

pH value :

It is the negative logarithm of the concentration of hydrogen ion (of base 10).

$pH = -\log [H_3O^+]$

The symbol (p) means (-log) .

This is a way for expressing the degree of acidity or alkalinity for aqueous solution. Referring to the ionic product of water and using the negative logarithm of this equation, the above relation becomes:

$-\log K_w = (-\log [H^+]) + (-\log [OH^-]) = -\log 10^{-14}$

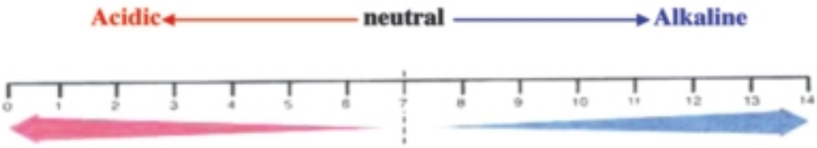
Substituting the value (-log) by the symbol (p) , the above equation becomes :

$pK_w = pH + pOH = 14$

In case of a neutral solution, the pH=7 and pOH =7.

For a solution of pH 5 , the pOH=9 and for a solution has a pH 8 , the pOH =6.

Consequently , the pH value of the acidic solutions is < 7 and the pOH is >7 and for basic solutions the pH is >7 and pOH is <7.



The following table illustrates the pH values of some solutions .

	Substance	PH
Acidic	1 molar solution of HCl	Zero
Acidic	0.1 molar solution of HCl	1.0
Acidic	Gastric solution	1.6 – 1.8
Acidic	Lemon juice..	2.3
Acidic	Acetic acid (Vinegar).................................	2.9
Acidic	Orange juice	3.5
Acidic	Grape juice..	4.0
Acidic	Tomato juice..	4.2
Acidic	Coffee...	5.0
Acidic	Rain – water...	6.2
Acidic	Milk..	6.3 - 6.6
Acidic	Urine...	5.5 – 7
	Neutral Pure Water	7.0
Alkaline	Saliva...	6.2 - 7.4
Alkaline	Blood...	7.35 – 7.45
Alkaline	Sea water...	8.4
Alkaline	Bile juice...	7.8 -8.6
Alkaline	Magnesia emulsion	10.5
Alkaline	0.1 Molar solution of ammonia.....................	11.0
Alkaline	Washing soda..	12.0
Alkaline	0.1Molar of sodium hydroxide solution..........	13.0
Alkaline	1 Molar solution of sodium hydroxide............	14.0

(The table is for illustration only)

Instrument to measure PH value

pH meter

Fig: 3-6

3. Hydrolysis of salt solutions :

Experiment: bring four test tubes , put a solution of sodium carbonate in the first, ammonium chloride in the second, ammonium acetate in the third and sodium chloride fourth. Test each solution with litmus paper . Record your observation and confirm the information that given in the following table,

Experiment	Observation	Conclusion
1. action of Na_2CO_3 solution	turns litmus blue	alkaline solution
2. action of NH_4Cl solution	turns litmus red	acidic solution
3. action of CH_3COONH_4	no action on litmus	neutral solution
4. action of NaCl solution	no action on litmus	neutral solution

These results can be explained as follows:

1. Hydrolysis of sodium carbonate: (a salt of a weak acid and a strong base)

Water is ionized as a weak electrolyte, giving hydrogen ions and hydroxyl ions and when sodium carbonate dissolves, it gives sodium ions and carbonate ions as shown by the following equations :

$$2H_2O_{(l)} \rightleftharpoons 2H^+_{(aq)} + 2OH^-_{(aq)}$$
$$Na_2CO_{3(s)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + 2Na^+_{(aq)}$$
$$Na_2CO_{3(S)} + 2H_2O_{(l)} \rightleftharpoons 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_2CO_{3(aq)}$$

In this reaction carbonic acid, sodium and hydroxide ions are formed. Sodium hydroxide is not formed because it is a strong electrolyte, completely ionized. Carbonic acid is formed due to the reaction between hydrogen ions (from ionization of water) and carbonate ions in the solution to give carbonic acid ,it is a weak acid, almost not ionized. Therefore, continuous hydrogen ions are formed from water causing a disturbed equilibrium . In order to attain a equilibrium according to Le Chatelier's principle, other molecules of water are ionized to compensate for the decrease in hydrogen ions. Consequently hydroxyl ions are formed accumulated and increased in concentration, to a level greater than the concentration of hydrogen ions giving a pH >7. Thus , sodium carbonate solution is alkaline.

2. Hydrolysis of ammonium chloride : (a salt of a strong acid and a weak base):

The solubility of ammonium chloride in water is represented by the following equations :

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$
$$NH_4Cl_{(S)} \rightleftharpoons Cl^-_{(aq)} + NH_4^+{}_{(aq)}$$
$$NH_4Cl_{(S)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)} + NH_4OH_{(aq)}$$

It is clear from this reaction ,that hydrogen ions, chloride ions and ammonium hydroxide are formed by dissolution of ammonium chloride in water. Hydrochloric acid is not formed, because it is a strong electrolyte, completely ionized (H^+, Cl^-). The presence of chloride ions (Cl^-) doesn't affect water equilibrium , but ammonium ions react with hydroxyl ions (OH^-), resulting from the ionization of water, to give ammonium hydroxide (a weak electrolyte). Due to the formation and consumption of hydroxyl ions from water, the equilibrium is

shifted. According to Le Chatelier principle, other (new) molecules of water are ionized to compensate the decrease in hydroxide ions and to reach a state of equilibrium. Consequently, hydrogen ions are formed , accumulated and exceeds the concentration of hydroxyl ions. Thus, ammonium chloride solution becomes acidic.

3. Hydrolysis of ammonium acetate (a salt of a weak acid and a weak base):

Solubility of ammonium acetate in water is represented by the following equations:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$
$$CH_3COONH_{4(S)} \rightleftharpoons CH_3COO^-_{(aq)} + NH^+_{4(aq)}$$
$$\overline{CH_3COONH_{4(S)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + NH_4OH_{(aq)}}$$

Both acetic acid and ammonium hydroxide are formed. Both are weak electrolytes. The concentration of hydrogen ions formed from the ionization of the weak acid is very small, and equals the concentration of hydroxyl ions formed by ionization of the weak alkali. Thus ,the solution is neutral .

4. Hydrolysis of sodium chloride : (Salt of a strong acid and a strong base):

The solubility of sodium chloride in water is represented by the following equations :

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$
$$NaCl_{(S)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$
$$\overline{NaCl_{(S)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)}}$$

Both hydrochloric acid and sodium hydroxide are strong electrolytes and completely ionized.

Therefore, hydrogen and hydroxide ions resulting from ionization of water remain constant and the solution is neutral.

From the previous we conclude that the hydrolysis process is opposite to the neutralization process. By dissolution of a salt in water, the acid and alkali from which the salt is derived are formed. The acidic or basic properly of the salt solution depends upon the respective strength of both the acid and the alkali formed due to the solution of the salt in water.

4. Solubility product

At certain temperature each solid salt has certain limit for soluble in water

When it reached to this limit A dynamic equilibrium state between the solid substance (solute) and solution (solvent) is established and the solution is called saturated solution

Solubility of solid salts in water is very wide where solubility of potassium nitrate KNO_3 in water = 31.6 g / 100 ml at 20°C where solubility of silver chloride in water at same temperature = 0.0016 g /100 ml

Concentration of saturated solution for sparingly soluble salt at certain temperature is known as degree of solubility

The dissolution of the sparingly soluble lead II bromide$PbBr_2$ in water is given by relation :

$$PbBr_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Br^{-}_{(aq)}$$

In this case the law of mass action can be applied:

∴ The equilibrium constant is given by the relation:

$$K_{sp} = \frac{[Pb^{2+}][Br^{-}]^2}{[\,Pb\,Br_2]}$$

∵ The solid $PbBr_2$ concentration remains almost constant :

$$K_{sp} = [Pb^{2+}]\,[\,Br^{-}]^2$$

K_{sp} is known as solubility product .

Solubility product for any sparingly soluble ionic compound is the product of multiplication of the concentration (expressed as mole / liter) of its ions ,raised to the power of the number of ions, which exist in equilibrium with its saturated solution .

Example : If the degree of solubility of silver sulphate(Ag_2SO_4)is $1.4X10^{-2}$ mole / liter , calculate the solubility product of Ag_2SO_4

Solution :

$Ag_2SO_4 \rightleftharpoons$	$2Ag^+$ +	$SO4^{2-}$
1mol	2mol	1mol
$1.4X10^{-2}$	$2X1.4X10^{-2}$	$1.4X10^{-2}$

$Ksp = [Ag+]^2 \ [SO4^{2-}]$

$Ksp = [2X1.4X10^{-2}]^2 \ [1.4X10^{-2}] = 1.0976 X 10^{-5}$

Evaluation

QUESTION 1 :

Define the following :

1.Chemical equilibrium . 2.Pressure of saturated water vapor in air

3.Complete reactions . 4.Reversible reactions.

5.Rate of reaction . 6.Catalyst .

7.Law of mass action . 8.Le Chatelier's principle .

9.Solubility product . 10.Ionic product of water .

11.pH . 12.Ostwald law.

QUESTION 2 :

Put the letter (R) in front of reversible reactions and letter (C) in front of complete reaction :

a. $NaOH_{(aq)} + HCl_{(aq)} = NaCl_{(aq)} + H_2O_{(l)}$

b. $AgNO_{3(aq)} + BaCl_{2(aq)} = 2AgCl_{(s)} + Ba(NO_3)_{2(aq)}$

c. $2Cu(NO_3)_{2(s)} = 2CuO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

d. : $CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$ In closed vessel

QUESTION 3 :

Write on :

a-The rate of chemical reaction and the factors affecting it .

B-Equilibrium reaction and the factors affecting it.

QUESTION 4 :

How each of the following changes affect the concentration of hydrogen in the following equilibrium system :

$$H_{2(g)} + CO_{2(g)} \rightleftarrows H_2O_{(g)} + CO_{(g)}, \quad \Delta H = 41.1kJ$$

a. Addition of more CO_2 gas.

b. Addition of more water vapour.

c. Addition of a catalyst.

d. Increase the temperature.

e. Decrease the vessel volume.

QUESTION 5 :

In which of the following reaction do you expect an increase in % dissociation, by increasing the temperature:

$NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$; $\Delta H = (-)$

$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$; $\Delta H = (+)$

$N_2H_{4(g)} \rightleftharpoons N_{2(g)} + 2H_{2(g)}$; $\Delta H = (-)$

QUESTION 6 :

Which of the following solutions is acidic, alkaline or neutral .

a. Solution of a pH 3.5.

b. Solution of a pH 7.0.

c. Solution of a pH 4.0.

d. Solution of a pH 12.0.

QUESTION 7 :

Write the scientific expression indicated by the following sentences:

a. The reactions which proceed in both forward and backward directions and the reactants and products are continuously exist in the reaction medium. (.........) .

b. The change in the concentration of the reaction per time unit (......).

c. At a constant temperature , the rate of a chemical reaction directly proportional to the product of multiplication of the reactants concentration raised to the power of the number of molecules (.........).

d. If any of the factors affecting a system under equilibrium such as pressure, concentration or temperature undergo change , the equilibrium will shift in the direction which will oppose this change (.......) .

QUESTION 8 :

Mention an experiment to prove:

a. The effect of concentration on the rate of chemical reaction.

b. The effect of temperature on the rate of a reaction under equilibrium.

QUESTION 9 :

Calculate the value of equilibrium constant for the reaction :

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

When the concentration at equilibrium for $[N_2O_4]$=0.213 mole/liter , and $[NO_2]$=0.213 mole/ liter.

QUESTION 10 :

What is the ionization % of 0.13 molar acetic acid solution ?

the ionization constant of acetic acid = 1.8×10^{-5}.

QUESTION 11 :

Which solution of the following substances is acidic , basic or neutral ?

$(NH_4)_2CO_3$, KCl, NH_4NO_3 , $FeCl_3$.

QUESTION 12 :

Write the equilibrium constant (K_C) of the following reaction :

$CO_{(g)} + H_2O_{(v)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

$4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(v)}$

QUESTION 13 :

If the degree of dissociation of a weak organic monoprotic acid is 33% in a 0.2 mole/ liter solution, calculate the ionization constant (K_a) of this acid.

QUESTION 14 :

The following reaction has two equilibrium constant values at two different temperatures :

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI$ Kc =67 at 850 °C

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI$ Kc =50 at448 °C

Is this reaction exothermic or endothermic ? explain your answer .

QUESTION 15 :

Fill the empty spaces in the following table , provided that the ionic product of water $Kw = 1x10^{-14}$ at 25°C .

$[H^+]$	$[OH^-]$	pH	pOH
$1x10^{-11}$	....	....	....
....	$1X10^{-5}$	....	....
....	....	6	....
....	....	....	12

QUESTION 16 :

If the solubility product of barium sulphate ($BaSO_4$) Ksp= $1.1X10^{-10}$

Calculate the concentration of $[Ba^{2+}]$ in saturated solution.

QUESTION 17 :

If the degree of solubility of silver chloride (AgCl)is 10^{-5} mole / liter , calculate the solubility product .

CHAPTER FOUR

ELECTROCHEMISTRY

Objectives

After the student finish studying this chapter he can :

1) Explain the reactions occurring in galvanic cell and the rule of the salt bridge .
2) Declare the standard hydrogen electrode and its use in measurement of standard electrode potentials .
3) Calculate the electromotive force for galvanic cell .
4) Write the cell diagram of galvanic cell .
5) Measure experimentally some electrode potentials
6) Identify different types of galvanic cells.
7) Explain the reactions that take place during the metal rust specially iron
8) Declear how to protect iron from rusting.
9) Verify experimentally faradays laws.
10) Calculate the amount of deposited matter using Faradays laws.
11) Declare the products of electrolysis of solutions and melts of salts.
12) Write the reactions occurring at electrodes in electrolytic cells .
13) Distinguish between galvanic and electrolytic cells .
14) Identify the application of the electrolytic cells .
15) Know the value of electro chemistry in human's progress.
16) Know the value of scientists in progress of electro chemistry .

Electrochemistry

Introduction:

Electric energy is considered as the most important and safe form of energy for environment. Electrochemistry is interested to study the exchange conversion of chemical energy and electrical energy through oxidation and reduction reactions. In these reactions the electrons are transferred from one of the reacting substances to the other during the chemical reaction. The following experiment represents one of oxidation – reduction reaction.

Experiment:-

Dip a Zn-sheet in blue copper sulphate solution, Fig .(4 -1a).

You will notice red copper metal precipitated on the surface of zinc sheet, while Zn-metal dissolves in the solution , fig .(4-1b). If this is continued for long period, the blue colour of copper sulphate solution decreases and becomes colourless and the dissolution of (Zn) increases.

Fig :4-1b

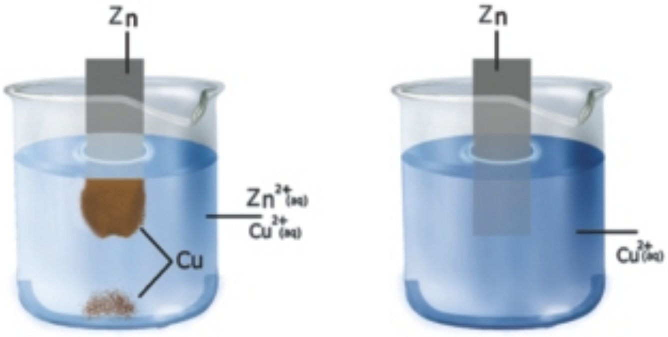


Fig :4-1a

This reaction is spontaneous redox– reaction and can be expressed by the following equation:

$$\overbrace{Zn_{(s)} + \underbrace{Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)}}_{\text{reduction}} + Cu^{0}_{(s)}}^{\text{Oxidation}}$$

We observe that this reaction consists of two half reactions:

<u>Oxidation reaction</u> : $Zn^{0}_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

In this reaction Zinc– atom (Zn^0) loses two electrons and converts to zinc ion (Zn^{2+}) dissolves and defused in the solution.

<u>Reduction reaction</u> : $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu^{0}_{(s)} \downarrow$

In this reaction copper ion (Cu^{2+}) in the electrolytic solution accepts two electrons (come from the Zn – half cell) and converts to copper metal (Cu^0) deposited on the surface of the Zn- sheet.

Scientists had succeeded in arranging a system known by galvanic cell consists of two half-cell their contents are found in isolated container connected together by a salt bridge, the electrons are allowed to pass through an electric wire between the half cells to obtain electric current produced from the spontaneous oxidation – reduction reaction which happens in the galvanic cell.

There is another kind of electric cells in which the electrical energy from an external source (dry cell) used to form oxidation – reduction reaction (nonspontaneous) .this kind of cells is known as electrolytic cells or electrolysis cell.

1- Galvanic cells

This is the kind of electric cells from which we can obtain electric current as a result of spontaneous oxidation – reduction reaction like the Daniell cell , shown in Fig .(4-2a) and fig (4-2b)

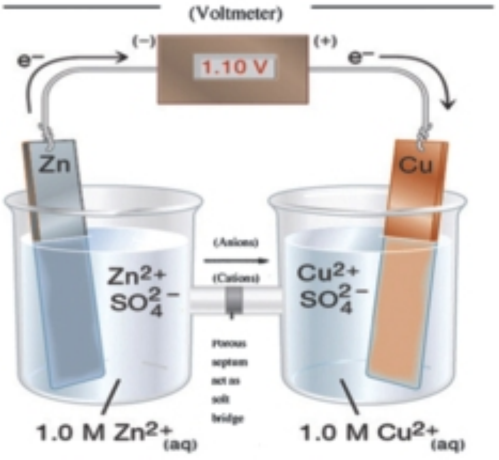


fig (4-2a)

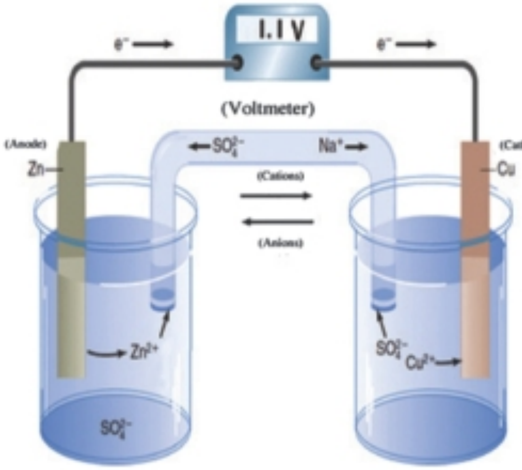


fig (4-2b)

This cell consists of copper plate (Cu-electrode) and zinc plate (Zn- electrode) each of them is dipped in one its salt solutions in two separate containers and they are connected together by a salt bridge. Copper plate is the cathode and it is the positive pole of the cell, while the zinc plate is the anode and it is the negative pole of the cell – the solution in each half cell is known as the electroyte. When the two electrodes of the cell are connected by a metal wire the electric current will pass. The oxidation – reduction reaction in this cell can be explained as follows:

A- <u>At anode</u>: $Zn^{o}_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$ oxidation

B- <u>At cathode</u>: $Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu^{o}_{(s)} \downarrow$ reduction

Total cell reaction occurring in cell Fig (4-2) is the sum of the two half- cell reactions.

Oxidation

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu^{0}_{(s)}$$

reduction

The flow of current is stopped between the two half cells when all of zinc metal dissolves in the zinc half-cell or all the copper ions disappear because they are precipitated as a copper atoms (Cu^0) in the copper half cell .

The galvanic cell for any two elements can be represented by a diagram as shown in the following:

$$Zn^{0} \,/\, Zn^{2+}_{(xM)} \,//\, Cu^{2+}_{(xM)} \,/\, Cu^{0}$$

Here a single bar indicates a junction between the electrode and the electrolytic solution of its ions , while the double bar indicates a junction between the two solutions in the two half cells (or salt bridge) .

You should notice that **oxidation** process occurs always at the **anode** while the **reduction** process occurs at the **cathode** in all electric cells.

***What is a salt bridge? What is its role in galvanic cells?**

The salt bridge in galvanic cells like (Daniel cell) is a glass U- shaped tube filled with strong electrolytic solution like (Na_2SO_4) its ions do not react with the ions present in the two half cells as well as with the electrode materials of the galvanic cell.

The salt bridge connects between the solutions of the two half cells indirectly. Also it neutralize the excess of both the positive and negative ions which forms in the solutions of the two half cells as a result of the oxidation and reduction reactions in zinc and copper half cells respectively. The absence of the salt bridge in the galvanic cell lead to stopping the oxidation and

reduction reaction and consequently stopping the flow of electric current in the external wire connecting between the two half cells .

Measurment of Electrode Potentials

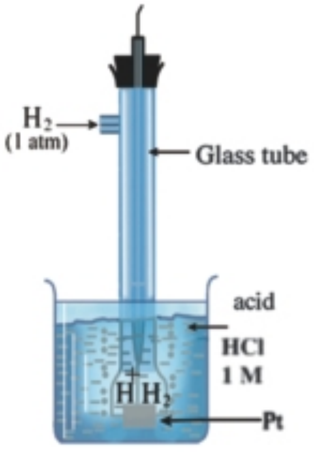


Fig :4-3

There is no certain and direct way for measuring the absolute electric potential difference between metal electrode and solution of its ions in galvanic cells while the difference between the two electrodes potentials of the galvanic cell can be easily measured. This is by forming of galvanic cell from two electrodes, one of them is the electrode that required to measure its potential and the other is standard electrode which has a constant known potential. Then measure the electromotive force of the cell (cell potential) is measured and from it the unknown electrode potential can be calculated.

Scientists had agreed to use the standard hydrogen electrode as a standard electrode, the potentials of other electrodes can be measured.by knowing its potential equals **zero** volt,

The standard hydrogen electrode as shown in fig (4-3) consists of a platinum sheet ($1cm^2$) covered by a layer of black spongy platinum over which a flow of hydrogen gas at constant pressure of one atmosphere passes and dipped in a molar concentration (1mol/L) of any strong acid solution .

The hydrogen electrode at such conditions is known as the standard hydrogen electrode (SHE) its potential = zero volt.

It courses the potential of this electrode changes by changing the hydrogen ion concentration in the solution or by changing the partial pressure of the hydrogen gas or both.

The standard hydrogen half-cell is represented by a diagram

Pt - H_2 (1 atm.) / $2H^+$ (1mol/L)

The ELECTROMOTIVE SERIES

Scientists had measured the standard electrode potentials (E^0) for all metals and nonmetals half cells relative to the standard hydrogen electrode.

If these standard potentials are descending arranged with respect to the negative reduction potentials and ascending relative to the positive reduction potentials, in which the more negative values are in the upper of the series and the more positive values are lower, we obtain what is known the electromotive series of elements. Which declares the following facts.

A- The elements which have the more negative values of reduction potentials and found at the top of this series are strong reducing agents and oxidized easily when they react with ions of any element in a lower position in the electromotive series.

B- The elements which have the more positive reduction potential which lie down in the series are strong oxidizing agents (when the metals are in ionic forms and the non-metals are in their elemental state), like fluorine molecules (F_2) . This means that it has more ability to accept electrons when it reacts with any element lies above it in the electromotive series.

C- The elements lie above in the series replace the elements which lie down in its salt solution and as the distance increase between two elements in series , the ability of the pre element (of most negative potential, or lower positive) to expel the following element (of lower negative potential or most positive) from its compounds .

D- All elements lie above hydrogen in the electromotive series replace hydrogen ions in acidic solutions (i. e hydrogen gas evolves).

Example : reaction of iron metal with hydrochloric acid

$$\overset{\text{Oxidation}}{Fe^0 + 2HCl \rightarrow FeCl_2 + H_2 \uparrow}_{\text{reduction}}$$

As the negative potential value increase, the ability to substitute hydrogen ions increases, while the positive potential elements which lie below hydrogen in the electromotive series cannot replace hydrogen ions in its solutions.

It is interesting to refer her that the standard half cell potential for any element takes negative or positive sign. If the reaction in zinc half cell as example is a reduction process, the potential here is known as the standard reduction potential (E^0) $Zn^{2+} + 2e^- \rightarrow Zn^0$ (reduction process)

And the **reduction potential** (E^o) of zinc half cell is pre estimated relative to the standard hydrogen potential as is found to equal – 0.76 volt , but the **oxidation potential** to this element has opposite sign since it represents here oxidation process . $Zn^0 \rightarrow Zn^{2+} + 2e^-$ $E° = +0.76$ v

Although it is also possible to arrange the electromotive series of elements according to the standard oxidation potentials in descending order relative to the positive potentials and ascending relative to the negative potentials. as shown in table (1)

The **electromotive force** of any galvanic cell can be calculated using the reduction or oxidation potential for the two half cells or both of them together where the potential of the galvanic cell always positive value .

The standard reduction potential for copper half cell = +0.34 volt

While the standard oxidation potential for copper half cell = - 0.34 volt

While the standard reduction potential of zinc half cell = - 0.76 volt

Where the standard oxidation potential of zinc half cell = + 0.76 volt

The electromotive force for the galvanic cell (emf) = the reduction potentials difference for the two half cells emf or E_{cell} = +0.34 – (-0.76) =1.1volt

emf = the oxidation potentials difference for the two half cells

emf or E_{cell} = 0.76 - (-0.34) = 1.1 volt

emf = summation of oxidation and reduction potentials of the two half cells

emf or E_{cell} = + 0.76+0.34 = 1.1 volt

The ELECTROMOTIVE SERIES of Elements

Half cell Half reaction	Standard oxidation potential (volt)	Standard reduction potential (volt)
$Li \rightleftharpoons Li^{+} + e$	+3.045	- 3.045
$K \rightleftharpoons K^{+} + e^{-}$	+2.924	-2.924
$Na \rightleftharpoons Na^{+} + e^{-}$	+2.711	-2.711
$Mg \rightleftharpoons Mg^{2+} + 2e^{-}$	+2.375	- 2.375
$Al \rightleftharpoons Al^{3+} + 3e^{-}$	+1.670	- 1.670
$Mn \rightleftharpoons Mn^{2+} + 2e^{-}$	+1.029	- 1.029
$Zn \rightleftharpoons Zn^{2+} + 2e^{-}$	+0.762	- 0.762
$Cr \rightleftharpoons Cr^{3+} + 3e^{-}$	+0.740	- 0.740
$Cr \rightleftharpoons Cr^{2+} + 2e^{-}$	+0.557	- 0.557
$Cr^{2+} \rightleftharpoons Cr^{3+} + e^{-}$	+0.410	-0.410
$Fe \rightleftharpoons Fe^{2+} + 2e^{-}$	+0.409	- 0.409
$Cd \rightleftharpoons Cd^{2+} + 2e^{-}$	+0.402	-0.402
$Co \rightleftharpoons Co^{2+} + 2e^{-}$	+0.280	-0.280
$Ni \rightleftharpoons Ni^{2+} + 2e^{-}$	+0.230	-0.230
$Pb \rightleftharpoons Pb^{2+} + 2e^{-}$	+0.126	-0.126
$H_2 \rightleftharpoons 2H^{+} + 2e^{-}$	Zero	Zero
$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^{-}$	-0.150	+0.150
$Cu \rightleftharpoons Cu^{2+} + 2e^{-}$	-0.340	+0.340
$4OH^{-} \rightleftharpoons 2H_2O + O_2 + 4e^{-}$	-0.401	+0.401
$Ag \rightleftharpoons Ag^{+} + e^{-}$	-0.800	+0.800
$Pt \rightleftharpoons Pt^{2+} + 2e^{-}$	-1.200	+1.200
$Au \rightleftharpoons Au^{3+} + 3e^{-}$	-1.420	+1.420
$2F^{-} \rightleftharpoons F_2 + 2e^{-}$	-2.870	+2.870

Table (1) [For illustration only]

GALVANIC CELLS AND PRODUCTION OF ELECTRIC ENERGY

The galvanic cells are divided according to their nature to produce electrical energy to:

1- **Primary cells.** 2- **Secondary cells**.

All of them are systems produce electrical energy through the spontaneous oxidation –reduction reaction.

1- Primary cells

These are saving energy systems in the form of chemical energy which can be converted to electrical energy through spontaneous irreversible oxidation reduction reaction. This kind of cells stops to work when the anode material is consumed and the ions of the cathode half- cell are diminished.

Primary cells not only easy but also impossible to be recharged to returning its constituents to its initial state this means that it is an irreversible cells. Of course for the easy use particularly in the mobile equipment, it should be in dry form not in liquid. Thus it is known as dry cells, and the cell in the dry form realize a constant potential for long time working in addition to the possibility of its manufacture in small size .We shall show as follows two of the important kinds of primary cells :

A- Mercury cell:

This cell is manufactured in shape of cylinder or disk – It is characterized by its small volume . Thus it is commonly used in ear phones , clocks and cameras – the negative pole is zinc and the positive pole is from mercury oxide – potassium hydroxide is used as an electrolyte and the cell is firmly closed , fig .(4-4) and the total reaction occuring in this cell .

$$\overset{\text{Oxidation}}{Zn^0 + HgO \rightarrow ZnO + Hg^0}$$
(Reduction)

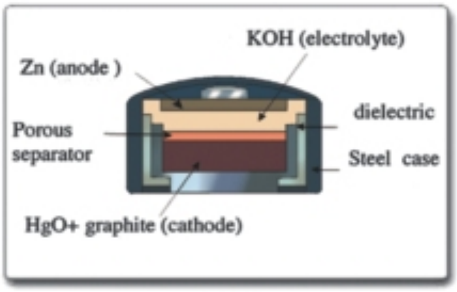


Fig4-4

This cell gives electromotive force $E_{cell} = 1.35$ volt ,
and it should get rid of this battery after using by a safe way since it contains mercury which is poison material.

B-Fuel cell:

It is known that hydrogen burns in oxygen of air strongly giving heat and light.

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(v)} + \text{Energy}$$

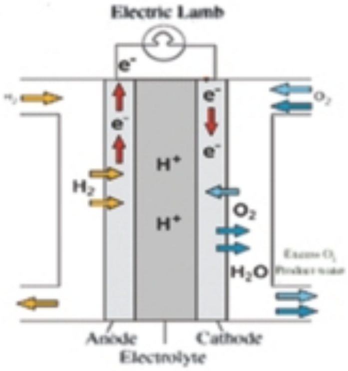


Fig4-5

The scientists could carry out this reaction under certain condition which can be controlled inside what is known by fuel cell. This type of cells is preferable in the space ships because its gaseous fuel (the mixture of hydrogen and oxygen) is the same fuel used in lunching rockets.

This cell is made from two poles, each of them is similar to a hollow container lined by a layer of porous carbon that connects between the internal room and the electrolyte that exists inside it which is hydrated potassium hydroxide.

The reactions in the fuel cell:

At anode (oxidation reactions):

$2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(v)} + 4e^-$ $E^\circ = 0.83V$ (oxidation)

At cathode (reduction reactions):

$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$ $E^\circ = 0.4V$ (reduction)

The total reaction:

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(v)}$ $E_{cell} = 1.23\ V$

The cell cannot be consumed like the other galvanic cells because it is supplied with fuel from an external source. Also it gives an electric current with emf or E_{cell} =1.23V.

It operates at high temperature and the produced water evaporate and can be condensed to be reused as drinkable water for the astronauts.

The fuel cell doesn't store the energy like the other batteries because its work requires a continuous supply with the fuel and a continuous remove of the products.

2- Secondary cells

These galvanic cells are characterized by reversible chemical reactions and store the electrical energy as chemical energy which can be converted once again to electrical energy when its needed and can be recharged by passing an electric current from an external source between their poles in a direction opposite to their discharge process. There are two examples of secondary cells.

A-Lead – Acid Battery :

This kind of batteries are developed and become the most suitable kind of batteries used in cars (so is known as car battery) .It consists of six cells are connected in series. Each cell produces $\mathbf{E_{cell} = 2}$ **volt** and the total cell potential of the battery is **emf = 2x6=12** volts and it is possible to manufacture large volume batteries contain more than six batteries when it is needed.

In this battery the **anode** is network of lead filled with spongy lead (Pb) (fig 4-6) and the cathode is lead network filled with a paste of lead dioxide (PbO_2) and the plates are separated from each other by insulting sheets and all of which are dipped in dilute sulphuric acid solution as a conducting electrolyte and all of which are put in a container made of solid rubber or plastic (polystyrene) which is not affected by acids and the battery works as a galvanic cell during its operation (discharge) and consuming its energy , while in the case of recharging it is considered as an electrolytic cell . fig (4- 6).

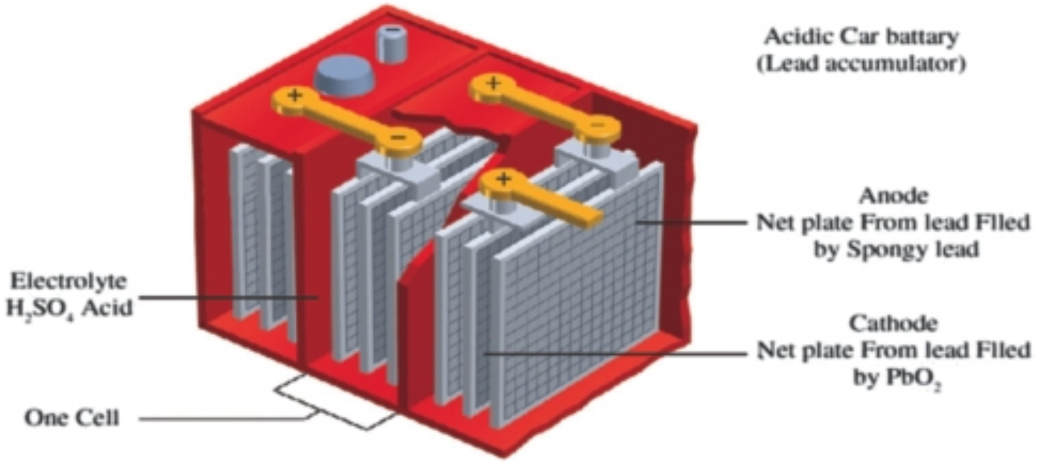


Fig . (4-6) the lead acid battery (lead accumulator)

A- Discharging reaction

these reactions occur during battery discharge :

At the anode :

$$Pb_{(s)} + SO_4^{2-} \rightarrow PbSO_{4(s)} + 2e^- \quad E=0.36V$$

(standard oxidation potential) = + 0.36 volt

At the cathode :

$$PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_{4(s)} + 2\,H_2O \quad E=1.69V$$

(standard reduction potential) = + 1.69 volt

The cell works here as a galvanic cell and at discharging the total battery reaction is :

$$Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_{4(aq)}^{2-} \xrightarrow{discharging} 2PbSO_{4(s)} + 2H_2O_{(l)} \quad E_{cell} = 2.05v$$

Exercise : calculate the electromotive force for this cell.

The battery state can be identified by measuring the density of the acid solution using the **hydrometer** (measuring liquids density) when the battery is completely charged. **The density of acid** equal from 1.28 to1.30 gm/cm^3 and if the acid density decreased to lower than 1.2 gm/cm^{-3} , this means that the battery needs to recharging and increasing its acid concentration .

B-Charging reaction

using the battery for long period leads to decrease the concentration of sulphuric acid as a result of increasing the quantity of water produced from the reaction and also leads to the conversion of cathode material (PbO_2) and anode (Pb) to lead (II) sulphate which lead to decrease of the quantity of electric current produced from it . Here the battery needs to be recharged and

this is done by connecting the battery poles to an outside source of direct electric current

Whose potential is slightly higher than the potential produced from the battery this will lead to the reversing of the spontaneous reaction which occurred during the discharge of the battery and lead to conversion of lead sulphate to lead at the anode and lead dioxide at the cathode and the concentration of the acid renewed as it was. .

$$\underset{(s)}{2PbSO_4} + \underset{(l)}{2H_2O} \xrightarrow{\text{charging}} \underset{(anode)}{Pb_{(s)}} + \underset{(cathode)}{PbO_{2(s)}} + \underset{(aq)}{2SO_4^{2-}} + \underset{(aq)}{4H^+}$$

The battery is working during charging as an electrolytic cell, where a nonspontaneous chemical reaction has occurred by passing electric current . This means the storage of electric energy which comes from the external source in the form of chemical energy. This is why the secondary cells are considered as storage batteries and in the car the dynamo in a continuous way is used in recharging the battery first by first.

B-Lithium ion battery:

It is a dry and rechargeable battery used in mobile, lap top the modern cars instead of the lead acid battery because it is lighter and store a large amount of energy while it is small in size.

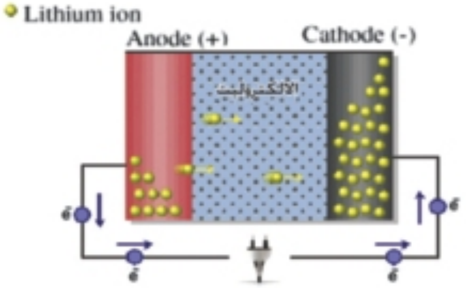
Its structure contains lithium because it is the lightest metal and it has the lowest reduction potential (-3.04V). the metallic cover of the battery contains three thin layers rolled in a spiral shape these layer are:

1- The cathode (+ve electrode) which is made from lithium \cobalt oxide ($LiCoO_2$)

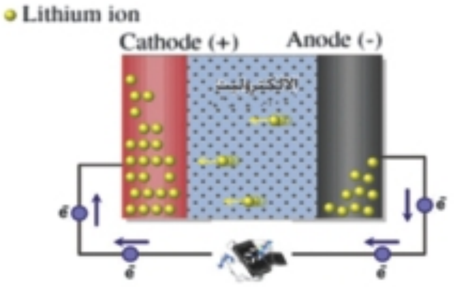
2- The anode (-ve electrode) which is made from lithium graphite (LiC_6)

3- The isolator which is made from a very thin layer of plastic which separate between the anode and cathode but it Allows for ions to pass through it.

These thin layers are dipped in anhydrous electrolytic solution of lithium Hexa Fluoro Phasphate ($LiPF_6$)



Recharge (Fig 4-7 B)



Discharge (Fig 4-7 A)

The following reactions take place during the operation of the battery:

At anode: $LiC_{6(s)} \longrightarrow C_{6(S)} + Li^{+}_{(aq)} + e^{-}$

At cathode: $CoO_{2(s)} + Li^{+}_{(aq)} + e^{-} \longrightarrow LiCoO_{2(s)}$

The total reaction: $LiC_{6(s)} + CoO_{2(s)} \underset{\text{Charge}}{\overset{\text{discharge}}{\rightleftharpoons}} C_{6(s)} + LiCoO_{2(s)}$

The emf of the battery $E_{cell} = 3V$

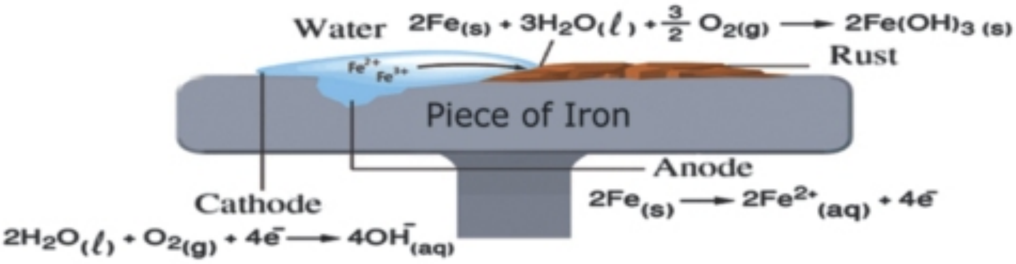
The corrosion of metals

Metal corrosion Cause heavy economic loss lead to deterioration of metallic structures, specially that are made of iron , the mass of iron that may be lost due to the corrosion can be estimated by one quarter of the production of the whole world every year . Hence the interest in this phenomenon and try to overcome and process chemical corrosion of metals by environmental effects is known as rusting.

The mechanism of corrosion:

In most cases the corrosion of the pure metals is difficult. Even iron doesn't rust easily in its very pure state, but most industrial metals are always contain different impurities that activate the corrosion process , the contact between less active metal to the more active metal causes corrosion for the more active in the same medium, then we can conclude that the corrosion of metals is formed due to the formation of galvanic cells in which the anode is the corroded element while the cathode which is the less active one or carbon that exists as impurities and this which causes corrosion.

Iron and steel corrosion mechanism can be explained as following:



Mechanism of Iron and Steel Rusting (Fig 4-8)

When a piece of steel is exposed to cracking or breaking it will form a galvanic cell with the water which contains dissolved ions that acts as electrolytic solution and iron acts as anode, the oxidation reaction takes place as following equation.

$$2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e^-$$

The iron ion Fe^{2+} becomes a part of the electrolytic solution and the electrons transfer through the piece of iron to the cathode (carbon impureties in iron) so iron acts as anode and external circuit.

At cathode the oxygen of air is reduced into a hydroxide group $(OH)^-$

$$2H_2O_{(\ell)} + O_{2(g)} + 4e^- \longrightarrow 4(OH)^-_{(aq)}$$

Iron ions Fe^{2+} are combined with hydroxide ions $(OH)^-$ to produce iron II hydroxide .

$$2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$

Iron II hydroxide will be oxidized by oxygen dissolved in water in to iron III hydroxide.

$$2Fe(OH)_{2(s)} + \frac{1}{2} O_{2(g)} + H_2O_{(\ell)} \longrightarrow 2Fe(OH)_{3(s)}$$

By addition of the previous equations we obtain the total equation for cell of iron corrosion.

$$2Fe_{(s)} + 3H_2O_{(\ell)} + 3/2\ O_{2(g)} \longrightarrow 2Fe(OH)_{3(s)}$$

The rust is a slow process due to the presence of limited amounts of ions in water and it increases if a big amount of ions exists in water as in sea water.

<u>The factors that causes corrosion:</u>

These factors can be classified into two kinds:

1- Factors specific to the metal itself. 2-Factors specific to the surrounding medium.

1- Factors specific to the metal itself:

a- Heterogeneity of alloys: the metals that used in industry mostly exist as alloys which are difficult to be prepared in homogenous structure , so a large number of local cells are formed which cause corrosion of the more active metal.

b- The connection of metals with each other: at points of welding metals together or using screws made from another metal, this causes the formation

of local galvanic cells causes corrosion of the most active metal , as in the contact between aluminum and copper, aluminum is corroded firstly and the contact between iron and copper, iron is corroded firstly.

2-The external factors (Factors specific to the surrounding):

Water, oxygen and salts are considered from the external factors that causes metal corrosion.

Protection of metal against corrosion:

The protection and preventing metals from corrosion specially iron, is considered from the bases of protection of the international economy.

In the following some methods of protection of iron against rusting, by covering it by another substance to insulate it from the surrounding medium this is happened by one of two methods:

1- Painting iron by the organic material like oil or varnish or primer but it is not effective method on the long run.

2- Covering iron by corrosion resistant metals like in steel galvanization process.

By dipping steel in molten zinc, also magnesium is used to protect steel used in ships industry , tin is used to protect iron that used in cans

a- Cathodic protection (Cathodic cover):

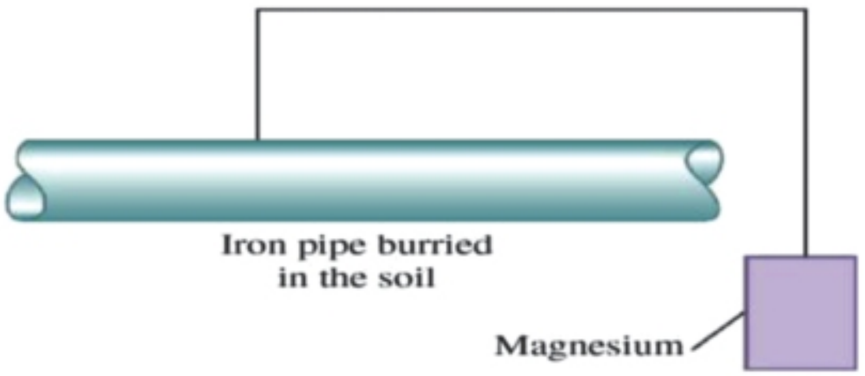
If the protective element is less active (like tin) than the original element (like iron) a galvanic cell is formed in which iron becomes more active metal and anode while tin becomes less active metal the cathode so iron corroded.

-Therefore, iron that plated with tin corroded on scratching faster than iron.

b-Anodic protection: (Anodic cover)

covering the metal by another more active metal such as plating iron by zinc (iron galvanization) where Zn precedes iron in the electromotive series ,then galvanic cell is formed in which Zn acts as anode so it is corroded completely first before starting of iron corrosion which takes a long time as iron corrosion begins at its surface, as ships chassis are continually in contact with

salty water and also iron pipes which are buried in moist soil so they are exposed more to corrosion , and can be protected by connecting them to the more active metal than iron like Mg which acts as anode, in this case Mg is corroded instead of iron and called sacrifying electrode.



Sacrifying Electrod (Fig 4-9)

Secondly : Electrolytic cells.

Electrolytic cells: are electric cells in which the electric energy from an external source is converted to chemical energy used through a nonspontaneous oxidation – reduction reaction. As shown in fig .(4-10) .It is a container contains electrolyte solution (like solution to any salt base , acid or molten of any salts) in which two electrodes of the same material (like carbon , or platinum) or each one of them is of different material (like carbon, platinum, copper, zinc or others) One of the electrodes is connected to the positive pole of the battery to become positively charged electrode at which oxidation reactions occur at (anode) , while the other electrode is connected to the negative pole of the battery and at which reduction reactions occur at (cathode) .It is interesting to note that electrolytes which are used as ionic

conductors in these cells are differ from electronic conductors (metals) . There are two kinds of liquid electrolytes .The first includes the solutions of acids , bases or salts and the second includes the molten of salts.

When the two electrodes are connected where the applied potential on the cell is slightly exceed the potential of the reversible cell, an electric current in the electrolytic cell flows and the positive ions in the electrolytic solution between the two electrodes are directed towards the negative electrode cathode) and neutralize their charge by accepting electrons (reduction) , while the negative ions from the electrolytic solution are directed towards the positive electrode (anode) and neutralize their charge by losing electrons (oxidation). If the electrolytic solution in this cell is copper chloride ($CuCl_2$) , the following oxidation – reduction reactions occur in the electrolytic cell :

a- **Oxidation reaction at the anode** (positive electrode)

$$2Cl^-_{(aq)} \xrightarrow{\text{oxidation}} Cl_{2(g)} + 2e^- \text{ (oxidation potential= -1.36 volts)}$$

b –**Reduction reaction at the cathode** (negative electrode)

$$Cu^{2+}_{(aq)} + 2e^- \xrightarrow{\text{reduction}} Cu^o_{(s)} \qquad \text{(reduction potential= +0.34 volts)}$$

and the total reaction occurs in the cell is the sum of the anode and cathode reactions .

Oxidation (anode)

$$Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightarrow Cu^o_{(s)} + Cl_{2(g)}$$

Reduction(cathode)

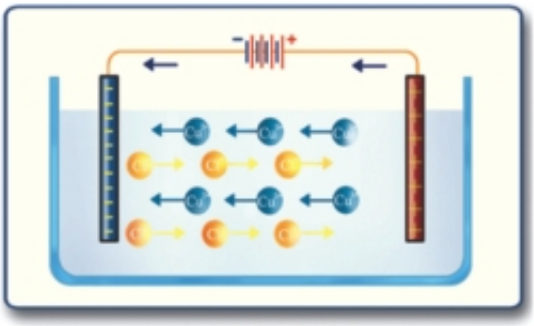


Fig : 4-10

Electrolytic cell for $CuCl_2$ solution

And the cell potential = sum of the oxidation and reduction potentials of the two half cells = -1.36+ 0.34 = -1.02 volts

The negative sign for cell potential means here that the total cell reaction occurring is non spontaneous if it was in a galvanic cell but it is completed in electrolytic cell by using electrical energy from an external source .And the process in which the separation of electrolyte solution constituents is completed (e.g evolution of chlorine and deposition of copper) is called electrolysis .

The electrolysis: It is a chemical decomposition of the substance due to the effect of passing electric current in the electrolyte.

Faraday`s Laws of Electrolysis

From the previous we find that, we can use the flow of electricity in the electrolytes and the neutralization of ions of these solutions in many industrial and laboratory applications to put a scientific basis for these process *Faraday had summarized the relationship between the quantity of electricity which flow in solution and the quantity of material librated at electrodes in two laws called by Faradays laws.

Faraday's First Law

The quantity of material (gas or solid) formed or consumed at any electrode is directly proportional to the quantity of electricity that passes in the electrolyteic (solution or molten).

Verify Faraday's First Law

By passing different quantities of electricity in the same solution and calculating the ratio of masses of the formed materials at the cathode or dissolved from the anode and comparing these ratios by the ratios of the passed quantities of electricity .

Faraday's second Law

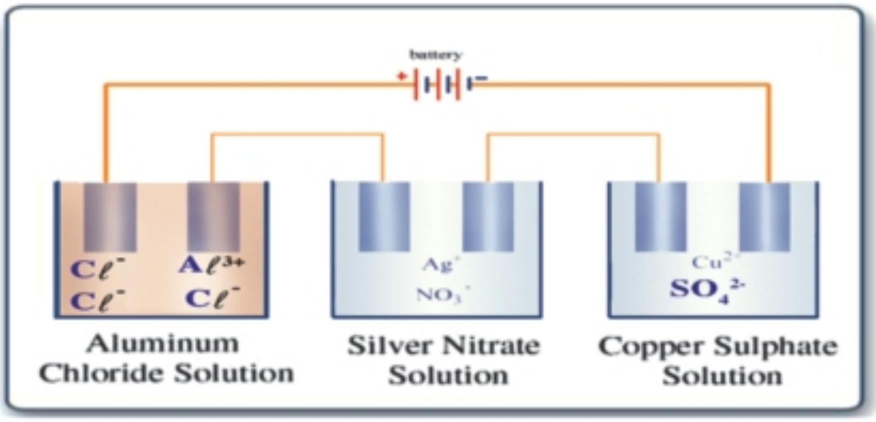
The masses of the different materials formed or consumed by the same amount of electricity that passes in different electrolytes connected in series are proportional to their equivalent masses.

Faraday's second Law can be expressed mathematically as:

$$\frac{\text{the mass of the first element}}{\text{the mass of the second element}} = \frac{\text{the equivelent mass of the first element}}{\text{the equivelent mass of the aecond element}}$$

The gram equivalent mass of the substance is themass of the substance that has the ability to lose or gain one mole of the electrons during the chemical reaction.

$$\text{The gram equivalent mass} = \frac{\text{the gram atomic mass}}{\text{number of charges on the ion of the element (Z)}}$$



Electrolysis of different elecrtlytic Solutions (Fig 4-11)

Verify Faraday's Second Law

The validity of these second law by passing the same quantity of electricity in different groups of solutions such as copper II sulphate, silver nitrate and aluminum chloride, (Fig 4-11)

The masses of the formed materials at the cathode in the cells of aluminum, copper and silver, respectively are proportional to their equivalent masses i.e in the ratio Al : Cu ; Ag = 9 : 31.78: 107.88 respectively . The quantity of electricity in coulomb that passed equal the result of multiplication of current intensity that used (in ampere) by the time (in seconds) through which the current passed .

Quantity of electricity (coulomb) = current strength (ampere) x time (second)

[1 C = 1 AX 1 S]

Faraday :

On passing a quantity of electricity of 1C in a solution of silver ions, a 1.118 milligram of silver are precipitated

on Passing 1C in $AgNO_3$ solution $\longrightarrow$ 0.001118 g of Ag precipitated

on Passing 1F in $AgNO_3$ solution $\longrightarrow$ 107.88 g of Ag gram equivalent mass precipitated

$$1F = \frac{1x107.88}{0.001118} = 96500\ C$$

It is clear from this , that the precipitation or dissolution gram equivalent mass of silver requires 96500 C and it is also at the same quantity of electricity

required to deposit or to dissolve the gram equivalent mass of any other element , according to faradays second law . this quantity is called the **faraday unit** , where one faraday (F) =96500 C .

General Law of electrolysis which is:

When one faraday(1F) (96500C) passes through an electrolyte, this will lead to dissolution or evolution or deposition of gram equivalent mass of the substance at any electrode.

Since the gram atomic mass of the substance equals the product of the gram equivalent mass multiplied the number of charges of its ions. Thus the faraday unit necessary to deposit gram/atom of the substance equals the faraday multiplied by the number of charges of the ion (Z), thus the quantity of electricity necessary to deposit gram/atom of silver according to the reaction :

$Ag^{+} + e^{-} \longrightarrow Ag^{\circ}$ equals to (1F).

And the quantity of electricity necessary to deposit gram/ atom of copper according to the reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu^{\circ}$ equals (2 F)

And in general the mass of deposited substance can be calculated by the following relationship mass of deposited substance (in gram)

$$= \frac{\text{current strength(amperes)x time(seconds) xequivalent mass of deposited substance}}{96500}$$

Example (1):-

What are the masses of gold and chlorine produced by passing 10000 C of electricity in aqueous gold chloride solution , knowing that the reactions occuring at electrodes are :

$$Au^{3+}_{(aq)} + 3\bar{e} \longrightarrow Au^{\circ}_{(s)}$$

$$3Cl^{-}_{aq} \longrightarrow \frac{3}{2} Cl_{2(g)} + 3\bar{e}$$

Solution :-

Equivalent mass of gold $= \frac{196.98}{3} = 65.6631$ gram

Equivalent mass of chlorine $= \frac{35.45}{1} = 35.45$ gram

$\therefore$ mass of deposited gold

$$= \frac{\text{quantity of electricity(coul.) x equv.mass.of gold}}{\text{96500 coul}}$$

$$= \frac{10.000 \text{x } 65.66}{96500} = 6.8 \text{ gram}$$

mass of evolved chlorine $= \frac{10.000 \text{x } 35.45}{96500} = 3.67$ gram

Example (2) :-

What is the quantity of electricity (C.) necessary to separate 5.6 g of iron from solution of iron (III) chloride where the cathode reaction is :

$$Fe^{3+} + 3e^{-} \rightarrow Fe^{\circ} \qquad (Fe = 55.68)$$

Solution :

Equivalent mass of iron $= \frac{\text{Atomic mass}}{\text{Valence}} = \frac{\text{Atomic mass}}{3} = \frac{55.68}{3} = 18.56$ gm.

That's mean :

The deposited of 18.56 gm of iron is need to ,96500 coulomb.

And deposited of 5.6gm of iron is need to (x) coulomb

Quantity of electricity (C.) $= \frac{\text{mass of deposited substance x 96500}}{\text{Equivalent mass of deposited substance}}$

$$= \frac{5.6 \text{ x } 96500}{18.56} = 29116.37 \text{C}$$

APPLICATIONS ON ELECTROLYSIS

1- Electroplating

It is a process of formation of thin layer of certain metal on the surface of another metal to give it a nice shiny view or to protect it from corrosion. we find as example that some cars parts which are manufactured from steel are electroplated by a chromium layer to take a beautiful shape and also to protect it against corrosion –Also some healthy sanitary ware like, water taps and mixers are electroplated by chromium or gold. Also electroplating is used in raising the value of some cheap metals after plating by chromium or gold or silver.

If we take for example, the electroplating of a jug by a layer of silver, the surface should be firstly completely cleaned, then dipped in electrolyte solution contains silver ions (like silver nitrate) and a rod or column of silver metal is put in the solution-the Jug should be connected by the negative pole of the battery, thus it be comes a cathode and the silver metal column is connected by the positive pole, thus it becomes anode in a cell as shown in Fig- (4-12)

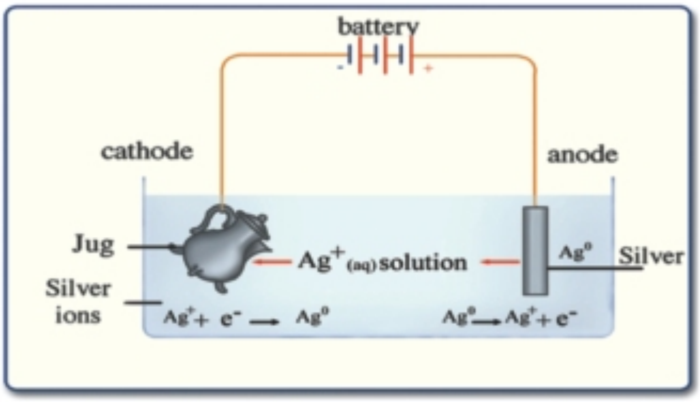


Fig 4: 12-4Electroplating by electricity

2- Extraction of aluminum

Aluminum is electrically extracted from bauxite (Al_2O_3) which is dissolved in cryolite melt (Na_3AlF_6) containing a little of fluorspar (CaF_2) to decrease the mixture melting point from 2045^0c to 950 ^{0}c

Recently **cryolite** is exchanged by using a mixture of **fluoride salts of Aluminum, Sodium and Calcium** where this mixture gives with bauxite a melt which is characterizes by a low melting point and a lower density value compared to the melt obtained from cryolite. The lowering of the melt density facilitates the melted aluminum separation which forms a deposited in the bottom of the electrolysis cell .

Fig .(4-13) represents a diagram of the used electrolysis cell.

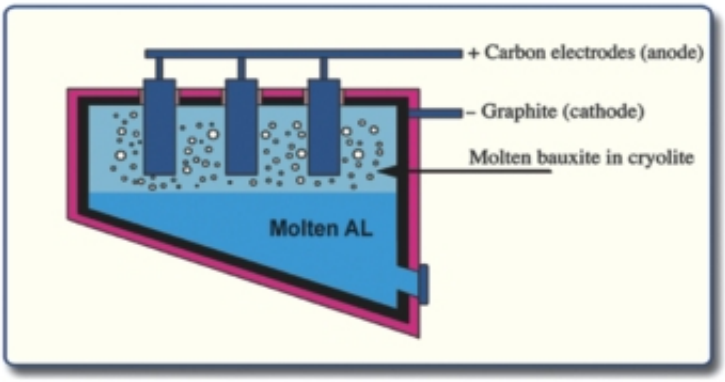


Fig :4-13 preparation of Aluminum by electrolysis

In this cell the cathode is the body of the cell container which is made from iron plated by layer of carbon (graphite) ,while the anode is carbon rods (graphite) . When the electric current passes between the cell electrodes an oxidation – reduction reaction occurs :

At the cathode (-) :

$$2Al^{3+} + 6e^- \xrightarrow{\text{reduction}} 2Al_{(l)}$$

At the anode (+) :

$$3O^{-2} \xrightarrow{oxidation} \frac{3}{2}O_{2(g)} + 6e^-$$

And the total reaction is :

$$2\,Al^{3+} + 3O^{2-} \longrightarrow 2Al + \frac{3}{2}O_2\,(g)$$

The evolved oxygen reacts with the carbon electrodes forming carbon mono and dioxides .

$$3/2O_{2(g)} + 2C_{(s)} \longrightarrow CO_{(g)} + CO_{2(g)}$$

Then aluminum is withdrawn from the cell through a special opening.

3- Purification of Metals

The degree of purity of metals which are prepared in industry is lower than the required degree of purity which is required for some specific applications. For example, copper of 99% purity contains iron, zinc, silver and gold impurities which decrease the ability of copper to conduct electrical and also its quality. Thus electrolysis method used for purification of copper that used in manufacturing electrical wires. The anode (positive pole) in the electrolytic cell is an impure copper metal (Cu^0) , while the cathode (the negative pole) is from wires or fine copper sheets and the electrolyte is an aqueous solution of copper sulphate as its molecules which dissociates in water to copper ions (Cu^{2+}) and sulphate (SO_4^{2-}) $CuSO_{4\,(aq)} \longrightarrow Cu^{2+} + SO_4{}^{2-}{}_{(aq)}$
when electric current passes from the external battery at a potential slightly more than the standard potential copper of half cell , the ions are directed towards electrodes which are opposite in the charge.

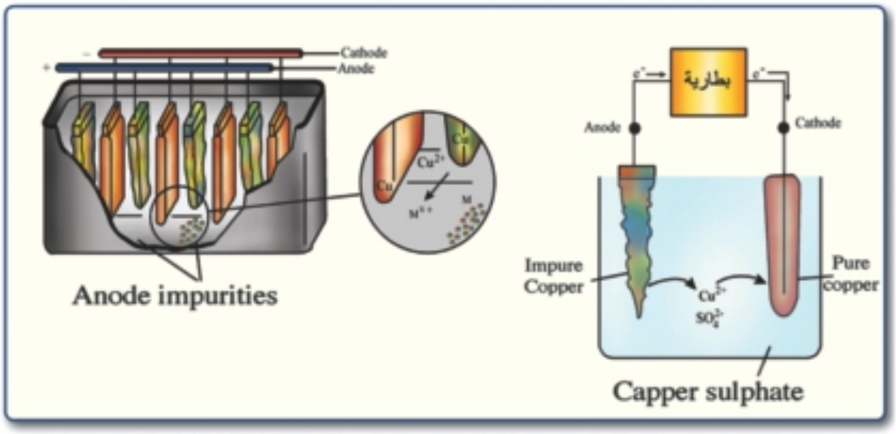


Fig 4-14 Purification of copper electrically

At the anode copper dissolves (oxidizes) and converts to copper ions (Cu^{2+}) which spread in solution and redeposit in the form of pure copper at the cathode.

At anode: $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$

At cathode: $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

While the impurities originally present in the anode material, some of them dissolve (oxidize) in the solution like iron and zinc but do not deposit at the cathode because they have lower reduction potential if it is compared to copper ions ,

$Zn^0_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

$Fe^0_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

While silver and gold impurities if it is present in the anode material it does not oxidize (do not dissolve) at the oxidation potential of copper and failed down the anode and removed from the bottom of the cell and by this method we can obtain 99.95 purity of copper. This is in addition to the possibility of separation of some rich minerals e.g gold and silver from copper ores as shown in F.g . (14-4)

Evaluation

QUESTION 1:-

Choose the correct answer between the two brakets :

1-Substances that conduct electric current through the movement of its ions are ………. conductors (metallic – electrolytic – electronic)

2-Systems in which the conversation of chemical energy to electrical energy is completed as result of occuring a spontaneous oxidation and reduction is…………(electrolytic cells – galvanic cells – solar cells) .

3-The electrode at which reduction process occurs in galvanic cells is…………. (Negative electrode – anode – cathode)

4-The electrode at which oxidation process in electrolytic cells occur is……… (Negative electrode – anode – cathode)

5-The moving material particles in melts or solution which are rich in electrons are (positive ions – negative ions- molecules) .

6-The standard hydrogen electrode has value of ……. (zero – positive – negative) .

7-When a quantity of electricity passes in electrolytic cells connected in series the masses of the formed elements at electrodes are proportional with …….. (atomic masses - atomic numbers – equivalent masses) .

8-If the standard reduction potentials for zinc and nickel were –0.76 and –0.23 volts , respectively - , thus emf for the cell is …………. Volt
[(0.99) / (0.76) / (0.53))] .

QUESTION 2:-

Answer the following :

1- Calculate the quantity of electricity in faraday that necessary to deposited gram – atom (mole) of aluminum during the electrolysis of Al_2O_3 (Al = 27) .

2- Calculate the mass of deposited calcium at the cathode as a result of passing an amount of electricity of 96500 coulomb in calcium chloride melt (Ca = 40) .

3- Write down the cell expression of the galvanic cell that formed from Sn^{2+}/Sn and Ag^{+}/Ag electrodes and calculate e.m.f if the standard reduction potentials for tin and silver are – 0.14 and 0.8 volts) respectively

QUESTION 3:-

Give reason for this :-

1- The importance of the fuel cell to the rockets.

2- The lithium battery is more preferable to the lead acid cell.

QUESTION 4:-

Write the reactions that takes place in:

a – Fuel cell

b- the lead –acid battery (charge and discharge)

c- Lithium ion battery.

d- Mercury cell.

QUESTION5:-

If you have a copper spoon what are the different steps you must follow it to plate it by a layer of silver – write down the equations (reactions) which occur at each of the cathode and anode .

QUESTION6:-

How we can obtain Aluminium from bauxite.

QUESTION 7:-

Pure copper 99% contains impurities. show how it can be purified from impurities to obtain 99.95 purity degrees.

QUESTION 8:-

Draw the cell diagram for the galvanic cell in which this reaction occurs :

$Ni^{2+}_{(aq)} + Fe_{(s)} \longrightarrow Ni + Fe^{2+}_{(aq)}$

Then show :

a. The cathode and anode.

b. The direction of current following

QUESTION 9:-

How many minutes necessary for the following:

a. Production of 10500 C from current of 25 A strength

b. Deposition of 21.5 g of silver from a solution of silver nitrate by passing a current of 10 amperes strength .

QUESTION 10:-

Calculate the quantity of electricity in faradays necessary to deposited 10 g of silver on the surface of a fork through electroplating process (Ag= 108) cathode equation (reaction)

$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(aq)}$

QUESTION 11:-

How can you obtain pure gold from a copper wire contains impurities of gold ?

QUESTION 12:-

Compare between each of the cathode and anode in the galvanic and electrolytic cells?

Chapter five

Organic chemistry

CH_4

CH_3-CH_3

CH_3-CH_2- CH_3

CH_3- CH_2- CH_2- CH_3

CH_3- CH_2- CH_2- CH_2- CH_3

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objectives

At the end of the study of this unit, student should be able to:

- Deduce that chemistry is an experimental science.
- Compare between organic and inorganic compounds.
- Distinguish between molecular and structural patterns.
- Draw different isomers for one molecular formula.
- Perform an experiment to detect the carbon and hydrogen in the organic materials.
- Classify hydrocarbon to its different types.
- Nomenclature of organic compounds by IUPAC system.
- Explain methods of preparing the hydrocarbon , writing the reaction equations and drawing the preparation apparatus
- Explain the economic importance of the hydrocarbon and their derivatives.
- Distinguish between the alcohols and phenols.
- Differentiate between the classification of alcohols according to the hydroxyl group and according to carbinol group attachment.
- Nomenclature of alcohol.
- Find the relation between alcohols and the other organic compounds like aldehydes, ketones and acids.
- Know the economic importance of alcohols.
- Practice an experiment to detect ethanol and phenol.
- Know the functional group to all acids and esters.
- Recognize the nomenclature of acids
- Recognize the properties of acids .
- Recognize the economic importance of acids and esters.
- Recognize the different kinds of organic reactions and how they contribute in the synthesis of our daily life products.
- Deduce that chemistry is a two-side weapon as it helps and destroy life.
- Appreciate the efforts of scientists in developing the science of organic chemistry

Organic chemistry

In the past, man used a lot of materials in his life which are extracted from the animals and plants as fats, oil, sugar, vinegar, alcohol and perfumes. Ancient Egyptians have used drugs in the mummification, dying, and fixed colours processes that still shine on their temples until now.

In 1806, the scientist Berzelius divided all compounds into two categories:

a) **Organic compounds**: They are compounds that extracted from animal or plant origin.

b) **Inorganic compounds**: They are compounds originate from mineral sources in earth.

Vital Force theory:

Berzelius considered that organic compounds are formed by vital force which is found in living cells of the body and it is impossible to synthesize them in laboratories.

In 1828, The German scientist **Wöhler** destroyed the vital force theory, when he prepared urea (organic compound formed in the urine of mammals) by heating an aqueous solution of two inorganic compounds, ammonium chloride and silver cyanate.

$$NH_4Cl_{(aq)} + AgCNO_{(aq)} \longrightarrow AgCl_{(s)} + NH_4CNO_{(aq)}$$

$$NH_4CNO_{\text{(Ammonium cyanate)}(aq)} \xrightarrow{\Delta} H_2N\text{-}CO\text{-}NH_{2\text{(Urea)}(s)}$$

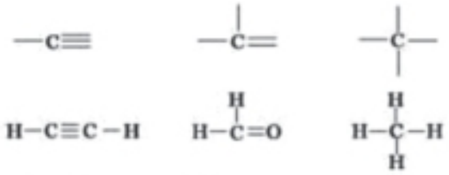
This experiment is considered a key event in the origin of organic chemistry. Chemists soon synthesized enormous organic compounds in all fields of life such as drugs, detergents, dyes, plastics, fertilizers and insecticides…..etc.

The organic materials become known according to their structure not according to their sources. This is because most of organic compounds which were prepared in laboratories are not formed in living organisms.

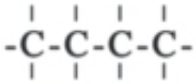
So, organic chemistry focused on the study of carbon element (with exception of carbon oxides, carbonate and cyanides salt.) Inorganic chemistry focused on the study of the rest of known elements i.e. someone may think that **the number of inorganic** compounds are more than the organic ones. **The opposite is right**. That the numbers of organic compounds exceed 10.000.000 and increase daily. The inorganic compounds don't exceed half of million. Therefore, the ratio between the organic and inorganic compounds is approximately 20: 1.

What are the reasons of the abundance of organic compounds?

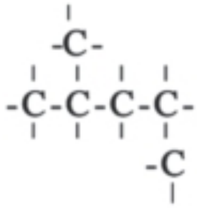
The abundance of organic compounds is due to the ability of carbon atom to combine with itself or with others atoms by different kinds of bonds , it might connect through single, double, triple bonds.



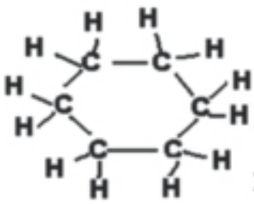
Carbon atoms can join together with different methods, straight chains, branched chains, homocyclic or heterocyclic.



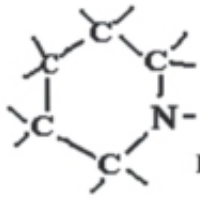
Straight chain



Branched chain



Homocyclic



Heterocyclic

The vast number and variety of organic compounds make scientists classify these compounds in groups which have less number of organic compounds and they put

the basis of its nomenclature. In the next section, we will focus on these groups and we will study their important chemical reactions. The aim of this study is to get an overview of some important topics in organic chemistry and its importance in our life.

The difference between organic and inorganic compounds

Practical experiment

Get some solid organic compounds (e.g. Paraffin wax**, Naphthalene**) and some liquid substance (e.g. ethyl alcohol, acetone, glycerol) and some inorganic liquid substances (e.g. water) and solid (e.g. table salt and copper sulphate).

Then, compare between the organic and inorganic compound concerning their solubility, melting point, boiling point, inflammability, odour and electrical conductivity.

From all the previous experiments, we make a comparison between the organic and inorganic compounds as shown in the following table.

Property	Organic compounds	Inorganic compounds
1-Chemical structure	- mainly contain carbon atoms.	may contain carbon atoms in addition to other elements.
2-Solubility	- most are insoluble in water but soluble in organic solvent e.g. benzene.	most are soluble in water
3-Melting point	- Low.	High
4-Boiling point	- Low.	High
5-The odour	-most have characteristic odour.	most are odourless
6-Inflammability	- inflammable and produce CO_2, H_2O	not inflammable, if it is inflammable it produces other gases
7-Kinds of bonds in the molecule	- covalent bonds	ionic bonds
8-Electrical conductivity	- don't conduct electricity.	Usually electrolytic compounds conduct electricity.
9-Rate of chemical reaction	- slow, because it takes place between the molecules	Often fast, because it takes place between the ions.
10-Polymerization	- can be polymerized	can't be polymerized
11-Isomerism	- it's found among many compounds	It is not found among their compounds.

The molecular and structural formula of organic compounds

Molecular Formula

It is the formula which indicates the number and kind of the elements atoms which form the chemical compound, and doesn't show the kind of the linkage between the atoms in the molecule.

Structural Formula:

It's the formula which indicates the number and kind of each elements atoms in the molecule, and the kind of linkage between the atoms by the covalent bonds. The number of covalent bonds around the atom indicates its valancy .Each single covalent bond represents one valence. Each element in the organic compound has a specific and constant valancy, where it is tetravalent in carbon atom, monovalent in hydrogen a, divalent in oxygen and trivalent in nitrogen.

Application:

Illustrate the structural formula of the following compounds:

Molecular formula	$C_2H_4Cl_2$	C_2H_4	C_2H_2	CH_3OH
Structural formula	Cl Cl | | H-C-C-H | | H H	H H | | C=C | | H H	H-C≡C-H	H | H-C-O-H | H

Isomerism

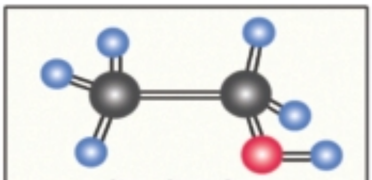
It is a phenomenon that many organic compounds are different in the physical and chemical properties and also in structural formula but they have the same molecular formula.

This is illustrated in the molecular formula C_2H_6O which represents two different compounds , they are ethyl alcohol and dimethyl ether.

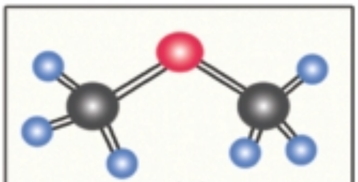
Molcular formula

C_2H_6O

	CH_3-CH_2-OH Ethyl alcohol	CH_3-O-CH_3 dimethyl ether
M.P.	-117.3°C	-138°C
B.P.	78.5°C	-29.5°C
Reaction with sodium	replaces hydrogen of hydroxyl group	does not react



CH_3CH_2OH



CH_3OCH_3

N.B.

On writing the structural formula it seems that the molecule has a planer shape, but in fact it has a stereostructure shape i.e. its atoms are directed in the three dimensions. To illustrate the correct shape of the molecule, we must use the molecular models which are different types, one of them is plastic balls having certain colours and sizes.

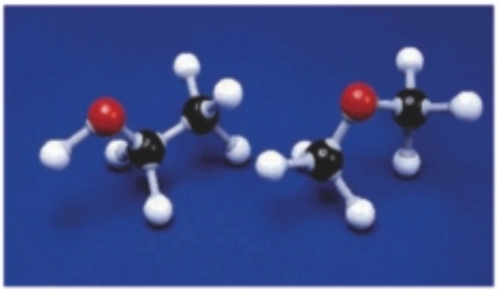
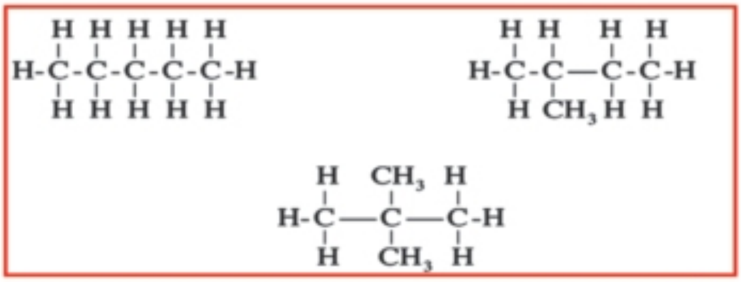


Fig: 5-1 Models of molecules

Exercise:

Draw the possible isomers of the molecular formula (C_5H_{12}) (form them using plastic molecular models).

The solution:

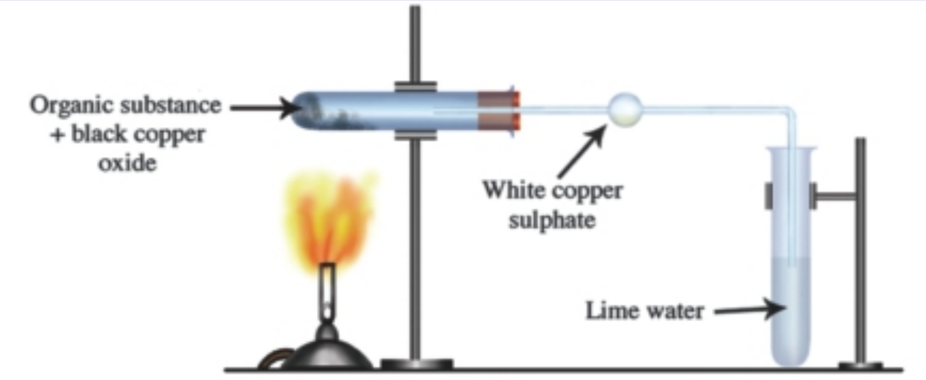


Detection of carbon and hydrogen in organic compounds:

Practical experiment:

Put a small amount of an organic substance (textile – leather – paper – plastic) mixed with copper oxide (CuO) in a glass tube that resists heat, heat the test tube strongly then pass the resulting gases over anhydrous white copper sulphate ($CuSO_4$), then through lime water (Fig. 5 – 2)

Record down your observation and conclusion then write the chemical equations.



(Fig. 5 – 2)

Observation:

1- The white colour of anhydrous copper (II)sulphate turns into blue which indicates the absorption of ($CuSO_4$) to water vapour which is formed from

combination of oxygen of copper (II) oxide with the hydrogen of organic compound.

2- Lime water turns turbid due to the evolution of carbon dioxide (CO_2), which is formed from combination of oxygen of copper (II) oxide with the carbon of the organic compound.

Conclusion:

The organic compound contains carbon and hydrogen.

$$C + 2CuO_{(s)} \xrightarrow{\Delta} CO_{2(g)} + Cu_{(s)}$$

$$2H + CuO_{(s)} \xrightarrow{\Delta} H_2O_{(v)} + Cu_{(s)}$$

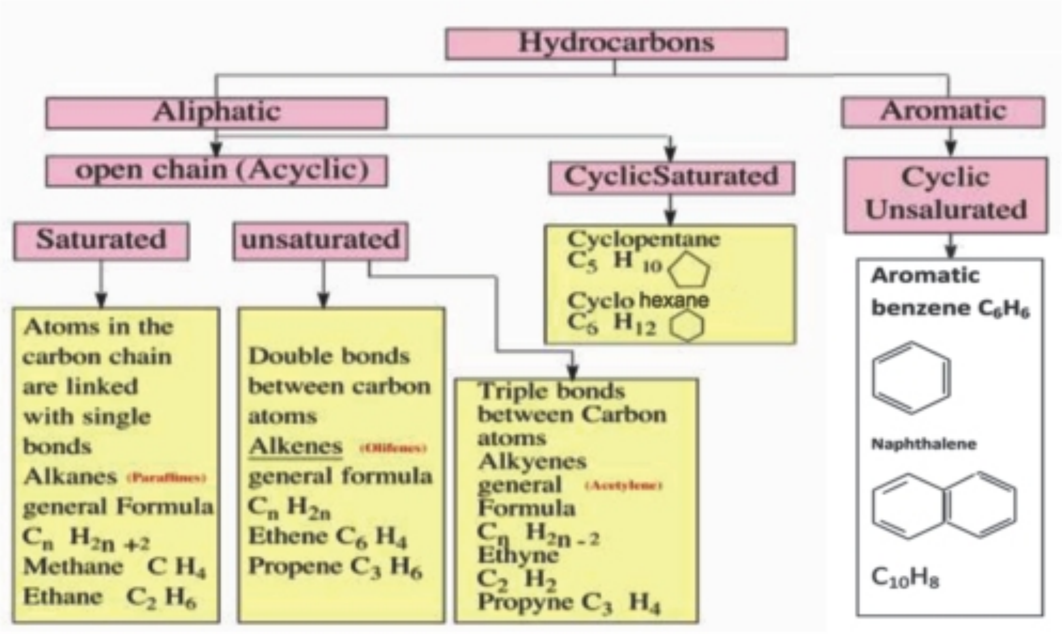
Classification of organic compounds

The backbone of organic compound is composed mainly of carbon and hydrogen forming what is called hydrocarbons, and the remaining compounds are known as hydrocarbon derivatives.

Hydrocarbons

They are organic compounds consist of carbon and hydrogen only.

They are divided into sub groups as shown in the following table.



Firstly: Aliphatic open chain hydrocarbons

Saturated aliphatic hydrocarbon:

Alkanes (Paraffins) (C_nH_{2n+2})

Alkanes are open chain hydrocarbons in which the carbon atoms are combined together by a single bond called sigma bond which is strong and difficult to be broken therefore they are relatively chemically inactive.

The following table shows the names and the formula of 1st 10 compounds in alkane's series.

Name	Formula	C_nH_{2n+2}
Methane	CH_4	CH_4
Ethane	CH_3-CH_3	C_2H_6
Propane	CH_3-CH_2- CH_3	C_3H_8
Butane	CH_3- CH_2- CH_2- CH_3	C_4H_{10}
Pentane	CH_3- CH_2- CH_2- CH_2- CH_3	C_5H_{12}
Hexane	CH_3- CH_2- CH_2- CH_2- CH_2- CH_3	C_6H_{14}
Heptane	CH_3- CH_2- CH_2-CH_2- CH_2- CH_2- CH_3	C_7H_{16}
Octane	CH_3- CH_2- CH_2- CH_2- CH_2- CH_2- CH_2- CH_3	C_8H_{18}
Nonane	CH_3- CH_2- CH_2- CH_2- CH_2- CH_2- CH_2- CH_2- CH_3	C_9H_{20}
Decane	CH_3- CH_2- CH_2- CH_2- CH_2- CH_2- CH_2- CH_2- CH_2- CH_3	$C_{10}H_{22}$

From the previous table we can observe the following:

1- All alkanes are characterized by the general formula (C_nH_{2n+2}),

Where (n) is the number of carbon atoms.

2- Each compound exceeds the previous one by (-CH_2) methylene group.

3- Members of this group are ended by the suffix (ane) which indicates that the compound is belonging to (alkane's chain), The prefix of the name indicates the number of carbon atoms in the molecule. For example the prefix Meth = 1 , Eth = 2 , Prop = 3 , But = 4 , Pent =5 and so on . Alkanes form a homologous series.

Homologous series:

It is a group of compounds that having the same general molecular formula , chemical properties and graduated physical properties like (boiling point).

Alkanes have a very important role as a fuel, starting materials for the preparation of many other organic compounds. Alkanes are found in large scale in the crude oil and they are separated by fractional distillation.

Methane represents (50 % to 90 %) of natural gas which is used now as fuel in homes. Propane and butane are compressed in cylinders and used also as a fuel. The long chain alkanes are found in kerosene, diesel, lubricating oils and paraffin's wax.

The Alkyl Radical (R –):

It is an organic atomic group which does not found alone. It is derived from the corresponding alkane by removing one hydrogen atom . Alkyl radicals are given the symbol "R". Their general formula is (C_nH_{2n+1}).Its name is derived from the corresponding alkane by replacing the suffix (ane) by (yl).

Examples	R-H Alkane $C_nH_{2n+2} \xrightarrow{-H}$ R- Alkyl radical C_nH_{2n+1}	
Methane CH_4	Methyl $-CH_3$	Methyl chloride CH_3Cl
Ethane C_2H_6	Ethyl $-C_2H_5$	Ethyl bromide C_2H_5Br
Propane C_3H_8	Propyl $-C_3H_7$	Propyl iodide C_3H_7I
Butane C_4H_{10}	Butyl $-C_4H_9$	Butyl chlorideC_4H_9Cl

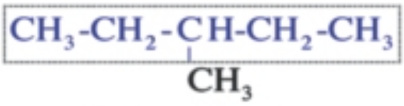
The nomenclature of alkanes (IUPAC system)

Ancient scientists use the name of the few organic compounds which are founding that time from the name of their sources in nature (common name),As the number of organic compound increases the nomenclature of the organic compound follows the (IUPAC) International Union of Pure and Applied Chemistry system.

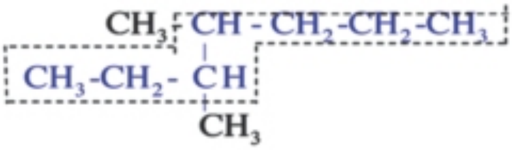
Anciently alkanes were called paraffins (common name).

The nomenclature of alkanes by the IUPAC system may be summarized as follows:

1- The name of the hydrocarbon is determined according to the longest continuous carbon chain which may be linear or branched.



Root name is pentane

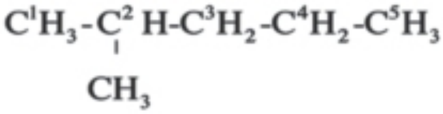


Root name is heptane

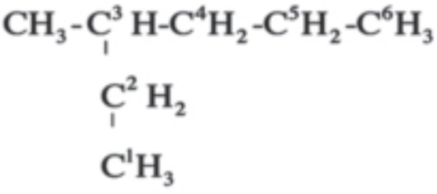
2- The carbon atoms are given numbers in the longest chain.

a- If the longest hydrocarbon chain free from any branches or side chain the carbon atoms are given numbers from any side (left or right side).

b- If the longest hydrocarbon chain attached to an alkyl group or any other atoms. The numbering of carbon atoms in the hydrocarbon chain begins from the side which is nearer to the branch. The nomenclature begins by the number of the carbon atom from which the chain arises, then the name of the branch, and ending by the name of the alkane.

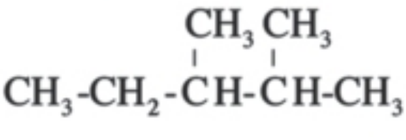


2-methyl pentane

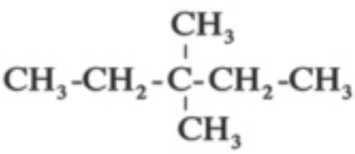


3-methyl hexane

3- If the side group is repeated in the hydrocarbon chain we use prefix Di – or Tri – or Tetra – to indicate the number of repetition.

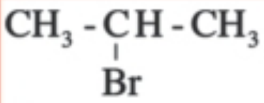


2,3 dimethyl pentane

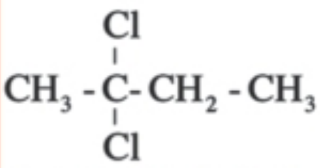


3,3 dimethyl pentane

4- If the branch is a group such as. Cl , Br or NO_2 , the name of this group is ended by the letter (O) so we say chloro , bromo or nitro.

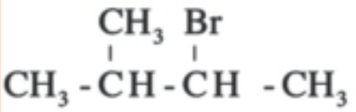


2 bromopropane

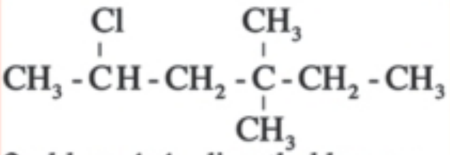


2,2 dichloro butane

5- If the side groups are different (alkyl group and halogens), the groups are arranged according to their alphabetical Latin names, after numbering from the end that giving the branches the least possible summation.

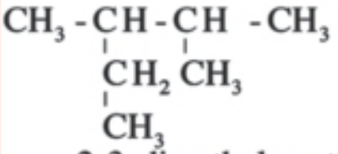


2, bromoro - 3 - methyl butane

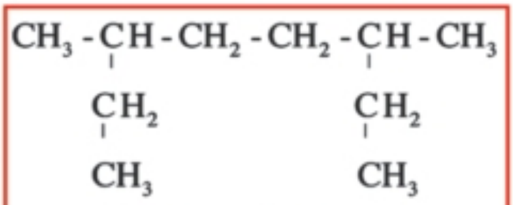


2,chloro 4,4 - dimethyl hexane

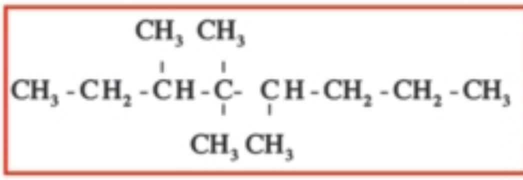
Exercise : **Name the following compounds using the IUPAC system.**



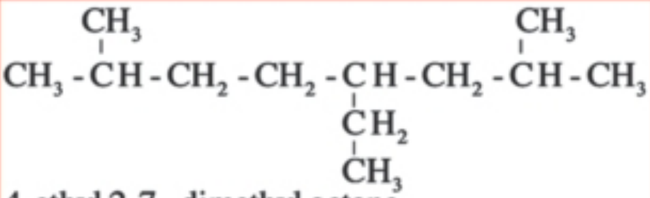
2,3, dimethyl pentane



3,6, dimethyl octane



3,4,4,5 - tetramethyl octane



4,ethyl 2,7 - dimethyl octane

CH_4 Methane

(A) Saturated open chain aliphatic hydrocarbons.

Alkanes (C_nH_{2n+2})

Methane is the first member, it is considered as the simplest organic compound and forms about 90 % of natural gas found under the earth's crust or accompanied to crude petroleum. Also, it is found in cool mines that may be exposed to an explosion as a result of its illumination .It is sometimes called the Gas of swamps "because it goes out as bubbles from the bottom of these swamps as a result of decaying of the organic matters.

Preparation of methane in lab. :-

Methane can be prepared in lab. by dry distillation of anhydrous sodium acetate with soda lime using an apparatus as shown in figure (5-2)

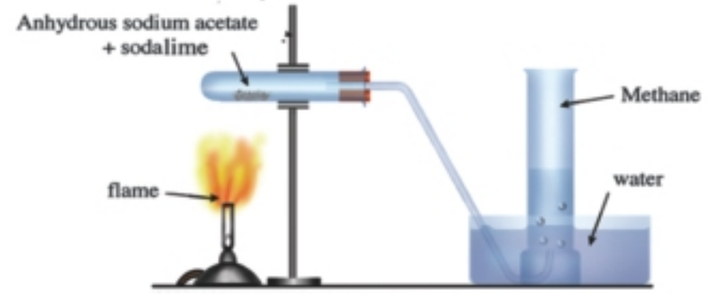


Figure 5-3

$$CH_3COONa_{(s)} + NaOH_{(s)} \xrightarrow{CaO\ /\ \Delta} CH_{4(g)} + Na_2CO_{3(s)}$$

Notice that **soda lime** is a mixture of **Na OH** and quick lime **CaO** which doesn't take part in the reaction but it helps in reducing the melting points of the reaction mixture .

The general properties of alkanes.

a) The physical properties :

1- The first four members of alkanes are gases in normal temperature. Methane can be used as fuel in homes, while the mixture of propane and butane, is filled in cylinders and is used as a fuel, Since propane more volatile (less boiling point) than , butane so we find that the ratio of propane is more in cold countries, while in warm countries the cylinders contain larger ratio of butane .

2- Alkanes ,which contain from 5-17 carbon atoms are liquids e.g gasoline and kerosine which are used as liquid fuel

3- The compounds which contain more than 17 carbon atoms are solids e.g. paraffin wax. i.e.: with increasing number of carbon atoms (molecular mass) in alkane, boiling point well increase.

4- Alkanes are non polar compounds insoluble in water, so the metals are covered by heavy alkanes like grease to protect them against rust and corrosion.

b) The chemical properties :

The carbon atoms in alkanes are combined together by the strong sigma bonds , These bonds cannot be broken easily except under certain conditions, Therefore, alkanes are comparatively, inactive compounds.

1-Burning : All alkanes burn giving water vapour and carbon dioxide, these reactions are highly exothermic, that is why they are used as fuels.

$$CH_{4(g)} + 2O_{2(g)} \xrightarrow{\Delta} CO_{2(g)} + 2H_2O_{(v)} + \text{Energy}$$

2-The reactions with Halogens:

Alkanes are react with halogens by heating up to 400°C or in presence of ultra violet rays in series of substitution reactions and the product depends up on ratio between methane and halogen in reaction mixture:

1- $CH_{4(g)} + Cl_{2((g)} \xrightarrow{(uv)} CH_3Cl_{(g)} + HCl_{(g)}$

Chloro methane (Methyl chloride)

2- $CH_3Cl_{(g)} + Cl_{2((g)} \xrightarrow{(uv)} CH_2Cl_{2(g)} + HCl_{(g)}$

Ddichloro methane (Methylene chloride)

3- $CH_2Cl_{2(g)} + Cl_{2((g)} \xrightarrow{(uv)} CHCl_{3(g)} + HCl_{(g)}$

Trichloro methane (chloroform)

4- $CHCl_{3(g)} + Cl_{2((g)} \xrightarrow{(uv)} CCl_{4(L)} + HCl_{(g)}$

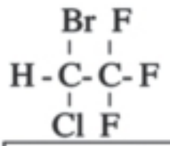
Tetrachloro methane (Carbon tetra chloride)

Exercise : **What are the products of the reactions of ethane with chlorine ?**

Write the structural formulae of the products.

Uses of halogenated derivations of alkanes :

1- Chloroform was used for a long time as anesthetic substance but its uses stopped because the inaccurate estimation of the dose for each patient causes the death. Halothane is used now as anesthetic substance with safety and its formula $CHBrCl - CF_3$



2-bromo -2-chloro -1,1,1-tri flouro ethane

2. The compound 1,1,1 trichloro ethane is used in the dry cleaning.
3. Freons were used in air conditions and fridges, also as a rushed substance to liquid and perfumes and as a cleaner of electronic sets.

Freons are consider as a kind of halogenated derivative of alkanes as CF_4 tetra flouro methane but the famous one is dichloro, diflouromethane CF_2 Cl_2 . Freons

are used by large quantities due to its sheep price, easily to be liquefied, non poisonous and non corrosive for metals, However Freon's cause the decay of the ozone layer which protect the earth against harmful effect of ultra violet rays . There is an international agreement to prevent their uses starting from 2020.

3.Thermal catalytic cracking:. This process usually takes place during the refining of petroleum oil to convert the heavy long petroleum chains (less used)to the daily used lighter short chain products .

This process takes place by heating the heavy petroleum products under high pressure and temperature in the presence of a catalyst to produce two kind of products:

a) Short chain alkanes which are used as car fuel like gasoline to fulfill the permanent world needs.

b) Short chain alkenes as ethene and propene which are used in many chemical industries such as manufacture of polymers .

$$C_8H_{18(l)} \xrightarrow{\text{high pressure ,temp,cat}} C_4H_{8(g)} + C_4H_{10(g)}$$

Octane butene butane

The economic importance of alkanes :

1-To obtain finely divided carbon, (black carbon).

The black carbon is produced by heating methane to 1000˚C in the absence of air.

$$CH_{4(g)} \xrightarrow[\text{no air}]{1000^{o}C} C_{(s)} + 2H_{2(g)}$$

Black carbon is used in the manufacture of car tiers, black painting, polishes, and printing ink .

2- To obtain " water gas" .

water gas is a mixture of hydrogen and carbon monoxide which is used as reducing agent or as a flammable fuel.

$$CH_{4(g)} + H_2O_{(v)} \xrightarrow{725^{o}C\ ,\text{cat.}} CO_{(g)} + 3H_{2(g)}$$

B-Unsaturated open chain aliphatic hydrocarbons.

Unsaturated open chain aliphatic hydrocarbons are classified into two groups :

1- Alkenes group : which are characterized by the presence of a double bond in the carbon chain .

2- Alkynes group : which are characterized by the presence of a triple bond in the carbon chain .

Alkenes (Olifenes) (C_nH_{2n})

They are unsaturated open chain hydrocarbons contain at least one double bond in the carbon chain. double bond contains a strong (Sigma) bond and weak (Pi) bond which is easily broken. This explain the activity of alkenes.

.They are considered as alkanes derivatives by removing two hydrogen atoms from the corresponding alkane. Therefore, they form a homogeneous series, Their general molecular formula is C_nH_{2n} .

Nomenclature of alkenes :

1- By using the same way in case of alkanes where we choose the longest continuous carbon chain .The suffix (ane) is replaced by the suffix (ene) in the name of alkene , preceding by the number of the carbon atom nearest to the double bond.

$CH_3 - CH = CH_2$ propene

$CH_3 - CH = CH - CH_2 - CH_3$ 2 – pentene

2- Numbering the carbon chain starts from the nearest side to the double bond regardless the position of other group.

$CH_2 = CH - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$

3 - methyl - 1 - pentene

$\underset{\underset{Cl}{|}}{CH_2} - CH_2 - CH = CH_2$ (4 - Chloro - 1 - butene)

==============

Ethene (C_2H_4)

The common name of ethene is ethylene, which is the first member of alkenes.

Preparation in lab :

Ethene can be prepared by removing water from ethyl alcohol by using hot concentrated (H_2SO_4) at 180°C as shown in figure (5-4).

$$C_2H_5OH_{(l)} \xrightarrow{\text{conc. (} H_2SO_4\text{) at 180°C}} C_2H_{4(g)} + H_2O_{(v)}$$

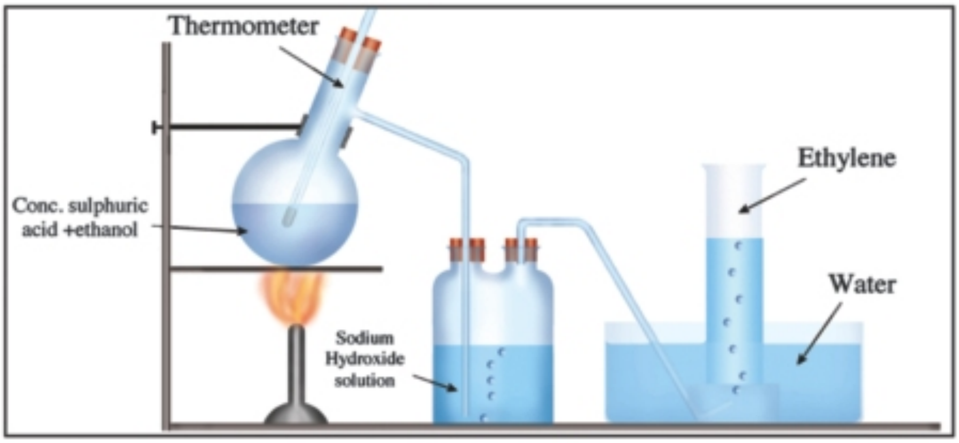
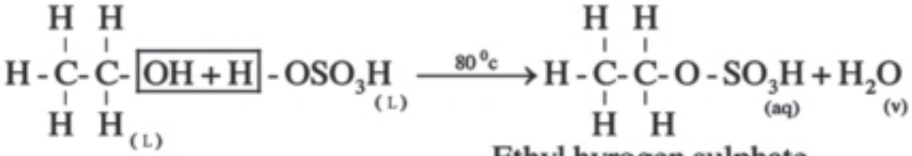


Fig : 5-4

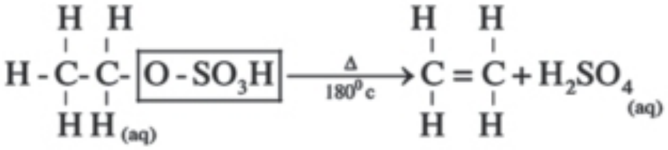
This reaction takes place in two steps.

1- Ethanol reacts with conc. heated sulphuric acid , to form ethyl hydrogen sulphate .



Ethyl hyrogen sulphate

2- Ethyl hydrogen sulphate thermally decomposed to give ethene .



$ethene_{(g)}$

Properties of alkenes :

The physical properties :

1- The first members of this series are gases. The alkenes containing 5 – 15 carbon atoms are liquids, those containing over (15) carbon atoms are solids .

2- Alkenes are non-polar compounds, insoluble in water but they can dissolve in organic solvents. Such as ethers, benzene and carbon tetrachloride.

Chemical properties :

Alkenes are more active than alkanes due to the presence of the weak (pi) (π)bond, which are easily broken.

1- Burning :

Alkenes burn in the air through exothermic chemical reaction giving carbon dioxide and water vapour .

$$C_2H_{4(g)} + 3O_{2(g)} \xrightarrow{\Delta} 2CO_{2(g)} + 2H_2O_{(v)} + \text{energy}$$

2- Addition reaction :

Alkenes are characterized by their ability to undergo addition reactions with other substances .The (Pi) bond is broken down and saturated compounds are formed .

a. Addition of hydrogen(H_2) (Hydrogenation) :

Alkenes react with hydrogen in the presence of a catalyst such as nickel or platinum with heating and the corresponding alkane is formed.

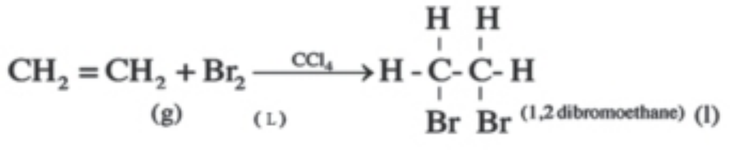
In each mole of hydrocarbon each pi (π) bond need mole of hydrogen to break it .

$$CH_2{=}CH_{2(g)} + H_{2(g)} \xrightarrow{\text{Pt or Ni at 150to300}^{o}\text{C}} CH_3\text{-}CH_{3(g)}$$

Ethane ethane

b. Addition of halogens (X_2) (Halogenation) :

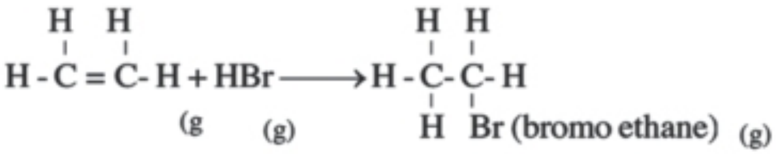
Halogens react with alkenes by additions, this reaction is used to detect unsaturated alkenes. When bromine in carbon tetrachloride is added to ethene, the red colour of bromine is removed and a colourless 1, 2 dibromo ethane is formed.



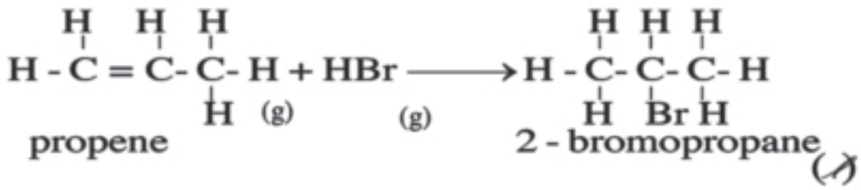
C. The addition of hydrogen halide (HX)

Alkenes react by addition with hydrogen halides where the (Pi) (π) bond break down. The hydrogen atom is added to one carbon atom of the double bond and the halogen atom is added to the other one, giving the corresponding alkyl halide. The addition products depend on the type of alkene.

a) If the alkene is symmetrical (i.e the two carbon atoms which are attached to the double bond carry the same number of hydrogen atoms), the hydrogen atom is added to any carbon atom and the halogen atom is added to other one .



c) If the alkene is asymmetrical (the two carbon atoms which attached to the double bond carries different number of hydrogen atoms) the hydrogen atom is added to the carbon atom rich in hydrogen atoms , whereas the halogen atom is added to the other carbon poor in hydrogen. This rule is known as "Markownikoff's Rule".



Markownikoff's rule :

"On adding an asymmetric reagent (HX or (H–OSO_3H) to an asymmetric alkene, the positive part of the reagent is added to the carbon atom which carries a large number of hydrogen atoms and the negative part is added to the carbon atom which carries less number of hydrogen atoms ".

d. Addition of water (H_2O) (Catalytic hydration) :

Since, water is a weak electrolyte, the concentration of hydrogen ions is very weak and is unable to break down the double bond .Therefore, the reaction should proceed in the presence of strong acid, to increase the concentration of hydrogen ions .Sulphuric acid is added firstly to form ethyl hydrogen sulphate which is hydrolyzed to give ethyl alcohol.

1- Addition of acid to ethene

$$\underset{(g)}{CH_2=CH_2} + \underset{(aq)}{HOSO_3H} \xrightarrow[80^\circ C]{\Delta} \underset{\text{ethyl hydrogen sulphate (aq)}}{CH_3-CH_2-OSO_3H}$$

2- hydrolysis of ethyl hydrogen sulphate

$$\underset{(l)}{CH_3-CH_2-OSO_3H} + \underset{(l)}{H_2O} \xrightarrow[110^\circ C]{\Delta} \underset{(l)}{CH_3-CH_2-OH} + \underset{(aq)}{H_2SO_4}$$

By addition

$$\underset{(g)}{CH_2=CH_2} + \underset{(l)}{H_2O} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{ethyl alchol (l)}}{CH_3-CH_2-OH}$$

3- Oxidation :

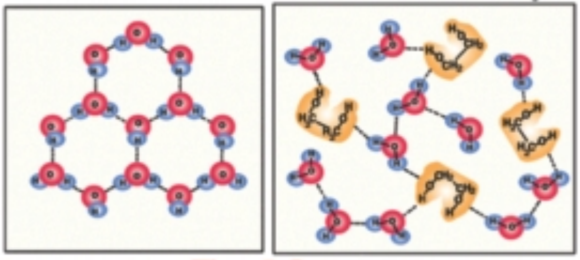
Alkenes are oxidized by oxidizing agent such as hydrogen peroxide (H_2O_2) or alkaline potassium permanganate $KMnO_4$ forming dihydroxy compounds known as glycols.

Baeyr's reaction :

It is the reaction between ethene and potassium permanganate in alkaline medium where the purple colour of potassium permanganate is discharged . This reaction is very important to detect the double bond.

$$\underset{(g)}{H-\overset{H}{C}=\overset{H}{C}-H} + \underset{(l)}{H_2O} + [O] \xrightarrow[\text{alkaline medium}]{KMnO_4} \underset{\text{(ethylene glycol) (aq)}}{H-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H}$$

Ethylene glycol is used as antifreeze substance which prevents the freezing of water in car radiators where it form hydrogen bonds with water molecule and prevent their combination with each other in the form of ice crystalsas in fig. (5-5)



Ice crystals Fig : 5-5 Water with ethylene glycol

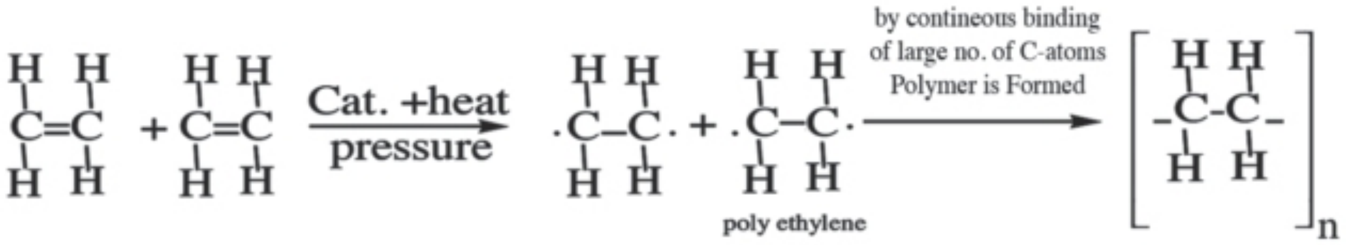
4- Polymerization :

The word polymer is a Latin word , means many – units. The polymerization process is the most important chemical reaction that enable to prepare several products which share in the flowering of civilization. Polymerization is the combination of a large number of compounds molecules (their number ranging from 100 to 1000,000) to form a huge molecule which has a big molecular mass. (The small primary molecule is called **monomer**, while the huge molecule produced from polymerization process is called **polymer**.

There are two principal methods for polymerization process.

1- Addition polymerization :

It takes place by adding a huge number of unsaturated small molecules to each other to form a very large molecule such as formation of polyethylene
Alkenes are characterized by their ability to form polymers by addition –
for example when ethene is heated under high pressure (about 1000 atmosphere) in the presence of Peroxides initiator,
poly ethylene is formed its molecular formula reach to about 30,000 (notice that the molecular mass of ethene = 28 only). In the addition polymerization of ethene (pi) bond is broken, the electrons of this bond are liberated .
Each carbon atom now has a free electron, then the carbon atoms of each molecule combine by their free electrons with those of other molecules by a single covalent bond to form a long chain of the polymer molecules.
This may be illustrated by the following equations:


Cat. +heat
pressure
poly ethylene
by contineous binding
of large no. of C-atoms
Polymer is Formed

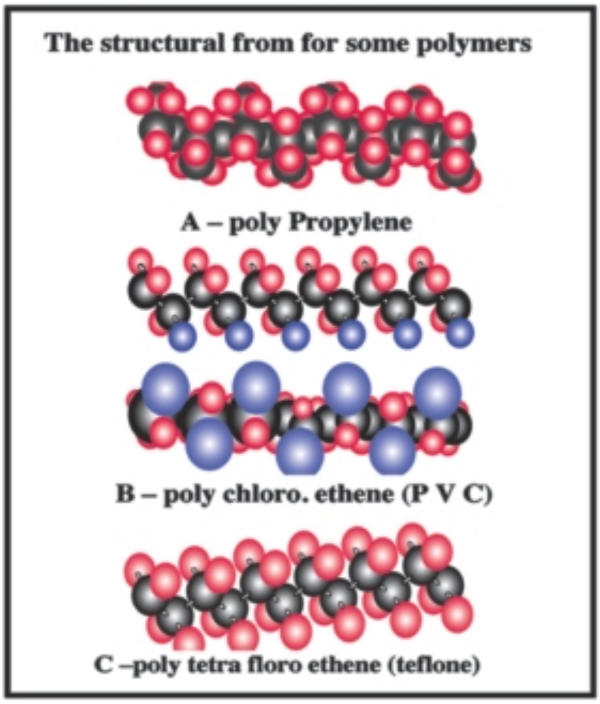
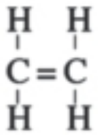
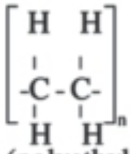
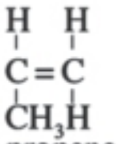
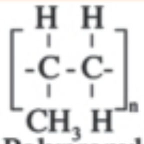
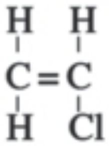
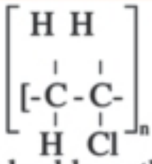
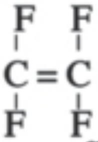
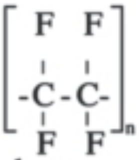

The structural from for some polymers
A – poly Propylene
B – poly chloro. ethene (P V C)
C –poly tetra floro ethene (teflone)

Fig: 5-6

The table illustrates some alkene monomers and their derivatives which are produced by addition polymerization and their uses:

Monomer	Polymer	Commercial name	Property	Uses
Ethene 	 (polyethylene)	Poly Ethylene (PE)	Soft and resist effect of chemicals	Plastic sheets, bags, bottles& hoses.
 propene	 Polypropylene (pp)	Poly propylene (PP)	Strong and hard	Carpets, cases and cans.
 Chloro ethene (vinyl chloride)	 Poly chloroethane	Poly vinyl chloride (PVC)	Strong and soft	Drainage tubes- plastic, tubes- shoes - hoses – electric wires, insulators – floors- oils bottles .
 tetra flouro ethene	 Poly tetra flouro ethene	Teflon	Resist heat and adhesion, electrical insulator and inert	Cooking utensils – surgical threads.

2- <u>Condensation polymerization</u> :

Condensation takes place between two different monomers and accompanied by losing a simple molecule such as water .

The copolymer formed is considered as the basic unit which continues the polymerization process, (we will study this kind in details later).

2- Alkynes (Acetylenes)C_nH_{2n-2}

They are unsaturated open chain hydrocarbons contain at least one triple bond in the carbon chain. They form a homogenous series its general molecular formula C_nH_{2n-2} . Each compound is less two hydrogen atoms than the corresponding alkene and four hydrogen atoms than the corresponding alkane. One of the triple bond is strong sigma bond ,while the other two bonds are weak (Pi) bonds . Therefore , alkynes are very active compounds.

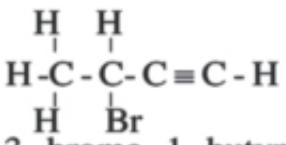
The first compound of this group is ethyne C_2H_2, its common name is a acetylene (this group is named by its name).

Nomenclature of Alkynes :

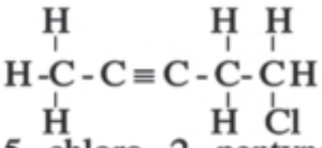
1- By using the same method used in the nomenclature of alkenes where. We choose the longest continuous carbon chain. The name of alkyne is derived from the name of corresponding alkane by replacing the suffix (ane) by suffix (yne).

2- Numbering the carbon chain starts from the end which is nearest to the triple bond whatever the position of any other branched group.

3- The name of alkyne is proceeding by the number of carbon atom which is attached to the triple bond.



3 - bromo - 1 - butyne



5 - chloro - 2 - pentyne

Ethyne (acetylene)

$H-C\equiv C-H$

Preparation in lab :

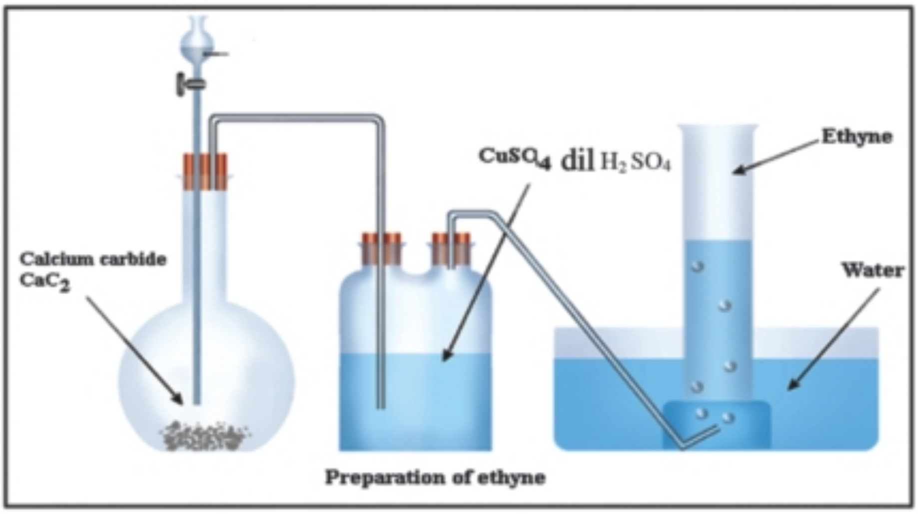


Fig.5-7

Water is dropped on calcium carbide (calcium dicarbide) using the apparatus shown in fig. (5-7). It is notice that before the collection of the gas it must be firstly passes over copper sulphate solution in dil sulphuric acid to remove phosphine gas (PH_3) and hydrogen sulphide H_2S . They are produced from the impurities found in calcium carbide.

$$\underset{\diagdown Ca \diagup}{C\equiv C}_{(s)} + 2\,HOH_{(l)} \longrightarrow H-C\equiv C-H_{(g)} + Ca(OH)_{2(aq)}$$

2-**Ethyne can be prepared in industry** from natural gas which contain high ratio of methane by heat to high temperature higher than 1400°C then fast cooling (**rapid quenching**) for the product

$$2CH_{4(g)} \xrightarrow[\text{rapid quenching}]{1500^{o}C} C_2H_{2(g)} + 3H_{2(g)}$$

Properties of ethyne :

1-Combustion : Ethyne burns with a smoky flame in air where oxygen is a limited amount because carbon does not completely burnt.

$$2C_2H_{2(g)} + 3O_{2(g)} \xrightarrow{\text{heat}} 2CO_{2(g)} + 2H_2O_{(v)} + 2C_{(s)}$$

In excess amount of oxygen ethyne is completely burned, producing carbon dioxide and water vapour through an exothermic reaction .

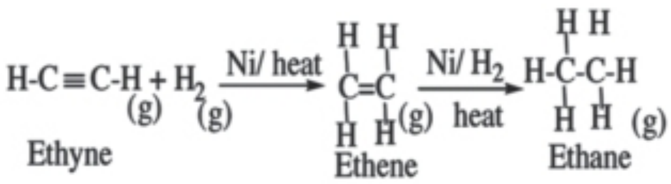
$$2C_2H_{2(g)} + 5O_{2(g)} \xrightarrow{\text{heat}} 4CO_{2(g)} + 2H_2O_{(v)} + \text{heat}$$

The amount of heat reaches about 3000°C, therefore oxyacetylene flame is used for welding and cutting metals.

2- Addition reactions :

Because ethyne contain two (Pi) bonds beside one sigma bond, it reacts by addition in two steps . The triple bond is changed to double and then to single bond. The addition reactions can be illustrated as follow.

a- Hydrogenation in the presence of finely divided nickel

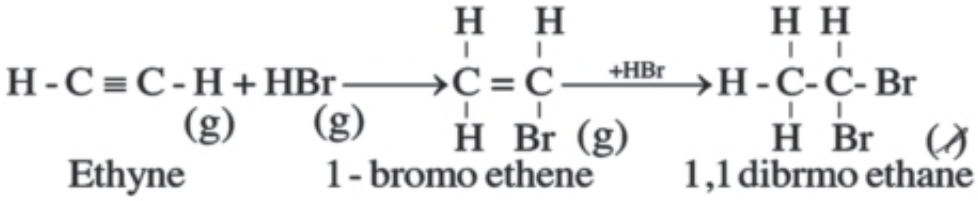


b- Halogenations : Ethyne reacts vigorously with halogens. The reaction may be accompanied by flame and light when it reacts with chlorine. However , when ethyne is passed through bromine water dissolved in carbon tetrachloride, the red colour of bromine is disappear. This reaction is used to detect the unsaturation of ethyne.

$$C_2H_{2(g)} + Br_{2(l)} \longrightarrow C_2H_2Br_{2(l)} \xrightarrow{+Br_2} C_2H_2B_{4(l)}$$

dibromo ethene   1,1,2,2 tetrabromo ethane

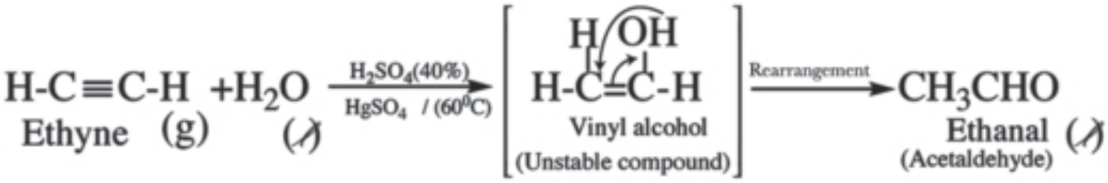
3-The addition of halogen acids (HX)



> Explain why1,2-dibromo ethane is not formed ....?
>
> (remember Markownikoff's rule)

4-Addition of water (catalytic hydration)

Ethyne reacts with water by addition in the presence of a catalyst e.g H_2SO_4, $HgSO_4$ at 60˚C to give acetaldehyde (ethanal).



This reaction is used to prepare ethanoic acid (acetic acid) by the oxidation of acetaldehyde (ethanal).

$$CH_3CHO_{(l)} \xrightarrow[\text{acidified } KMnO_4]{\text{Oxidation}} CH_3COOH_{(l)}$$

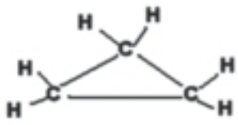
Ethanol can be obtained from reduction of acetaldehyde (ethanol)

$$CH_3CHO_{(l)} \xrightarrow[\text{(reduction)}]{H_2} CH_3CH_2OH_{(l)}$$

Secondly Cyclic hydrocarbons

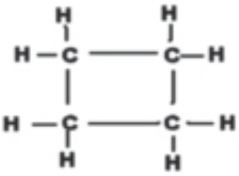
a- Saturated cyclic hydrocarbons (Cycloalkanes)

Hydrocarbons which contain three or more carbon atoms may found in cyclic structure. The general form of Cycloalkanes is C_nH_{2n} which is the same as the molecular formula of aliphatic alkenes. So we have to differentiate between them on writing their molecular formula.



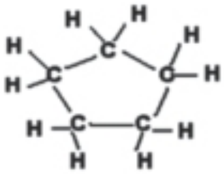
C_3H_6

Cyclopropane



C_4H_8

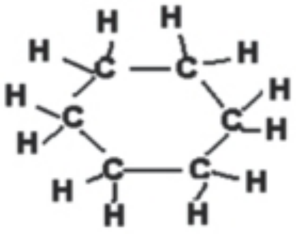
Cyclobutane



C_5H_{10}

Cyclopentane

Nomenclature of cyclic alkanes is similar to open chain alkane but we put the prefix "cyclo" in case of cyclic alkanes.



Cyclohexane C_6H_{12}

It is observed that the angles between the bonds in cyclopropane equal 60° while they are 90° in cyclobutane. They are less than 109.5° which is found in open chain alkanes. These small angles lead to weak overlap between the atomic orbitals. Therefore ,the combination between carbon atoms are very weak. They are very active for example cyclopropane forms with air an extremely burning mixture , while normal propane (linear propane) is less active. Cyclopentane and cyclohexane are stable because the angles between the bonds near 109.5°– so the overlap between the atomic orbitals becomes more strong therefore a strong sigma bonds are formed.

Unsaturated cyclic chain hydrocarbons(Aromatic hydrocarbons)

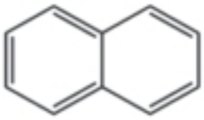
Ancient scientists differentiate between two kinds of organic compounds. Organic compounds derived from fatty acids which contain a high ratio of hydrogen , they are called aliphatic compounds (fatty), methane is considered the parent member of these compounds. The other organic compounds which are produced from some resins and natural products, having a characteristic odour, contain a less number of hydrogen atom are called "aromatic compounds". Aromatic benzene is first member of these compounds. The aromatic compounds may contain one , two or more benzene rings beside their various derivatives.

Exercise :

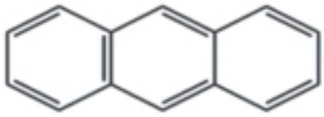
Write the molecular formula of the following compounds.

1-Aromatic benzene:

2-Naphthalene



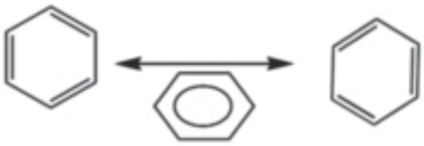
3-anthracene



> **N.B. :** Fuel used in cars is the gasoline which is completely different from aromatic benzene.

The structural formula of benzene

Identification of the structural formula of benzene took several years. It reacts by addition and by substitution. The bond length between the carbon atoms are intermediate between the length of single and double bond .In addition to other properties which made the scientists confused for a long time. In 1931 the German scientist **kekule** discovered the hexagonal cyclic shape in which single and double bonds are exchanged.



Benzene

i.e The ring in figure indicates that the 6 electrons are delocalized at certain carbon atoms.

Preparation of benzene in industry

1- From coal Tar :

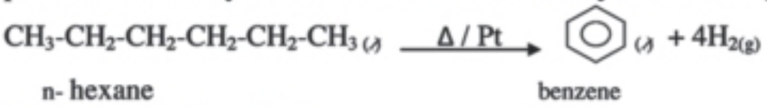
During destructive distillation of coal (heating in absence of air) it decomposes into gases and liquids. The most important of these liquids is a heavy black substance known as " coal tar ". By fractional distillation of coal tar, we obtain, very important organic compounds economically. Benzene is obtained at 80 - 82°C

2- From aliphatic petroleum derivatives :

Due to the importance of aromatic benzene as a starting material in chemical industries. It is possible to obtain it from aliphatic petroleum derivatives by two methods:

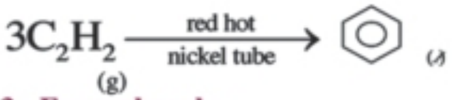
a) From normal hexane :

In this method, normal hexane is passed at high temperature on the surface of platinum as a catalyst. This method is called **catalytic reforming method**



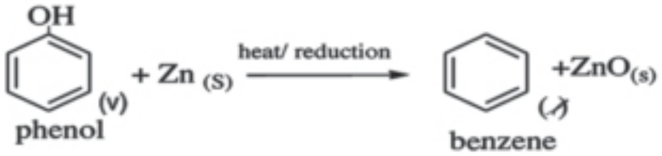
b) Polymerization of ethyne :

By passing ethyne vapour in a red hot nickel tube.



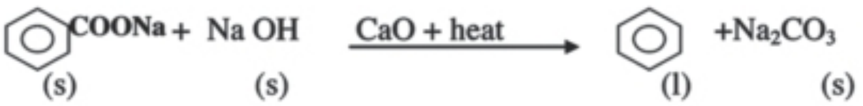
3- From phenol :

By passing phenol vapours on the surface of hot zinc powder which reduces phenol to benzene .



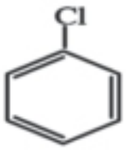
Preparation of benzene in lab.

Pure benzene can be prepared in lab. by dry distillation of sodium benzoate with soda lime (as in case the preparation of methane in lab).

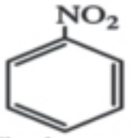


Nomenclature of benzene derivatives :

1- The name of mono-substituted benzene is derived from the name of the atom or the group which is attached to benzene ring followed by the word benzene.



Chlorobenzene



Nitrobenzene

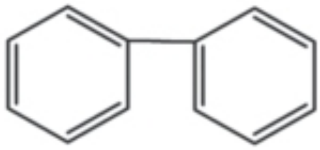
N.B. The entering atom or the group attacks any carbon atom of benzene since the six carbon atoms in benzene ring are identical.

The aryl radical (Ar)

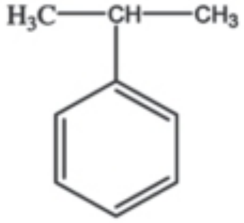
It is the radical which produce by removing one hydrogen atom from the aromatic compound (its symbol is Ar).

For example when we remove a hydrogen atom from benzene the produced radical is called phenyl radical (C_6H_5-)

Exercise: Nomenclature of some aromatic compound



Diphenyl C_6H_5-C_6H_5

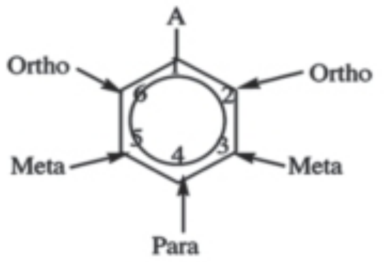


2-phenyl propane

What is the difference between diphenyl and Naphthalene?

Write the molecular formula for each of them.

2-The disubstituted benzene may be represented by three isomers which are: ortho (o-) , meta (m-) and para (p-).



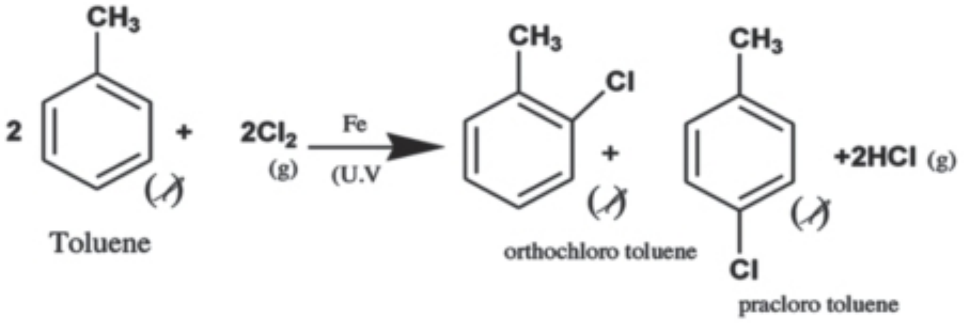
2,6 Ortho

3,5 Meta

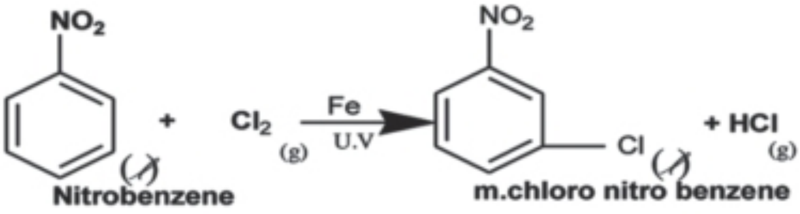
4 Para

The product depends on the nature of the substitutent group which is mainly found (A). There are some groups direct the new substituent to **ortho** and **para** positions and other direct to **meta** position.

From groups which is directed to ortho and para positions are the alkyl group(-R) , hydroxyl group(-OH), amino groups ($-NH_2$)and halogen atoms(X-).



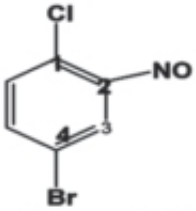
From the meta directing groups are the aldehydic group(-CHO), ketonic group (-CO), carboxylic group(-COOH) and Nitro group($-NO_2$).



3- If benzene is trisubstituted, it is impossible to use the expression ortho, meta and para .The carbon atoms in the ring take a numbers where each carbon atom attached to a group or atom takes the same number. The nomenclature is arranged according to alphabetical letter for example the bromine takes a number before

chlorine and chlorine before nitro group and so on, and numbering with lowest summation value.

N.B: Nomenclature by the IUPAC system, considers only the numbering of benzene ring.



4-bormo -1-chloro -2-nitro benzene

Physical properties of benzene

Transparent liquid, immiscible with water, it has a pleasant- smell, Its b.p is 80°C.

Chemical properties

It burns in air with a black smoky flame, this mean that its molecule contain a large number of carbon atoms.

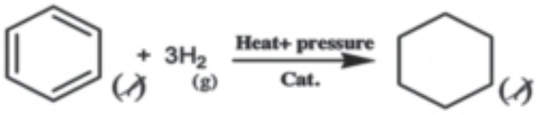
Benzene reacts by two kinds of chemical reactions (addition and substitution)

a) **Addition reactions :**

Although the molecule of benzene contains double bonds but its reactions by addition is difficult and takes place under certain conditions.

1- The addition of hydrogen (hydrogenation):

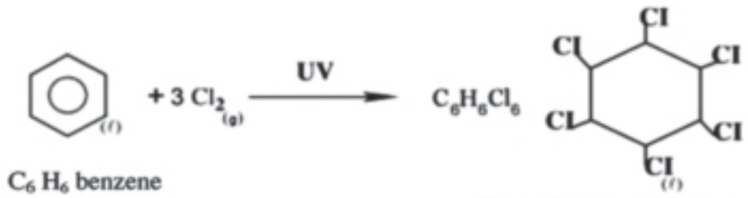
Benzene reacts with hydrogen under pressure and temperature , in the presence of catalyst to give cyclohexane,



C_6H_6 benzene C_6H_{12} Cyclohexane

2- Halogenation:

Benzene reacts with chlorine or bromine in sun light (uv) to form hexa halo cyclohexane, with chlorine an insecticide is formed which is called gamixane.

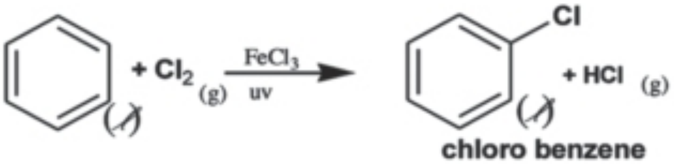


Hexa chlorocyclo hexane
(Gamixane)

b) **Substitution reaction** :

Substitution reactions are very important reactions because they produce very important economical compounds. In these reactions one or more hydrogen atoms are replaced by another atom or group.

1- Halogenation



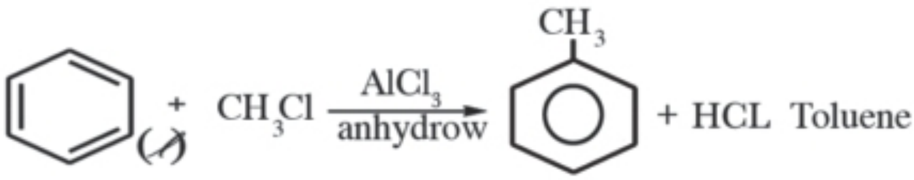
chloro benzene

In the previous reaction one hydrogen atom is replaced by one chlorine atom, when chlorine reacts with benzene in sun light (uv) in presence of iron III chloride as a catalyst to form chlorobenzene.

Aryl halides are produced in large scale and are used as insecticides , the most important one is D.D.T which is dichloro diphenyl, trichloro ethane . Its poisonous effect is due to the presence of the group (-CH-CCl_3) in the molecule which dissolves in the fatty tissue of the insect and kill it. it was called the ugliest compound in the history of chemistry for its environmental problems which appeared during its usage.

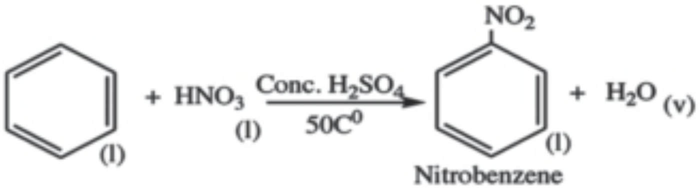
3- Alkylation (Friedel – craft's reaction):

Benzene reacts with alkyl halides (RX) where the hydrogen atom of benzene ring is replaced by an alkyl group forming alkyl benzene. This reaction usually takes place in the presence of anhydrous aluminum chloride ($AlCl_3$) as a catalyst.



2- Nitration

Benzene reacts with nitric acid in the presence of concentrated sulphuric acid, where the hydrogen atom of benzene ring is replaced by a nitro group(- NO_2)



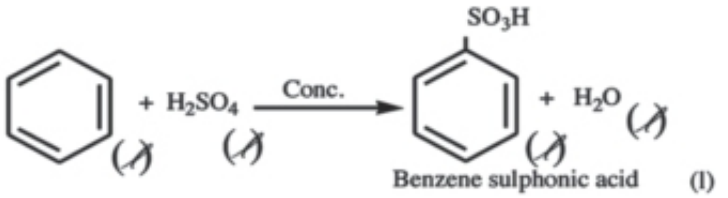
It is noticed that the poly nitro organic compounds are very explosive substance since their molecules contain their own fuel ,which is carbon beside oxygen which is the oxidizing agent . These compound burn rapidly, and a great amount of heat and gases are produced accompanied by explosion. This is due to the weakness of the bond between N and O (N – O) , to form the two strong bonds, between C and O (C – O) in carbon dioxide and the bond between (N – N) in nitrogen molecule.

The bond	Bond energy K J/mole
N - O	201
C = O	358
N ≡ N	941

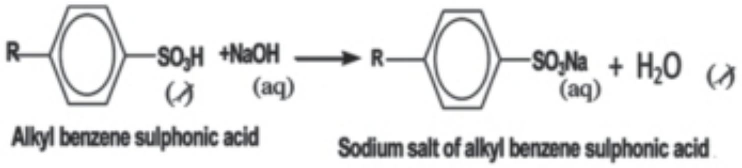
T.N.T (trinitrotoluene) is one of the explosive nitro organic compounds which was produced by millions of tons through the second world war , and still produced until now. This compound is prepared by the reaction between toluene and a mixture of concentrated Nitric and sulphuric acids (1 :1 ratio)

4- Sulphonation :

In this process the hydrogen atom of benzene ring is replaced by a sulphonic acid group (SO_3H). This usually takes place by the reaction between aromatic benzene and conc. sulphuric acid where benzene sulphonic acid is formed.

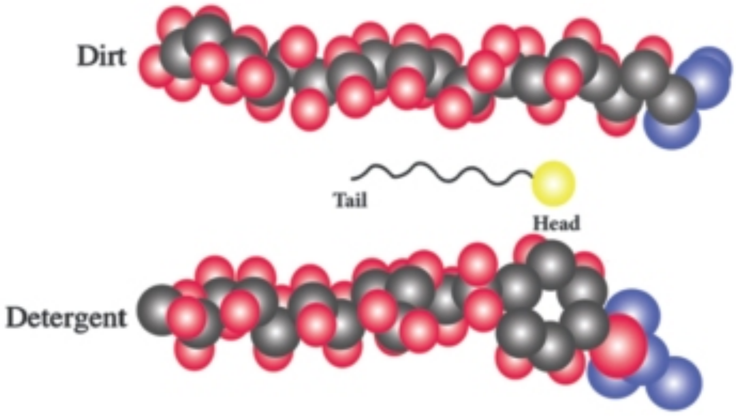


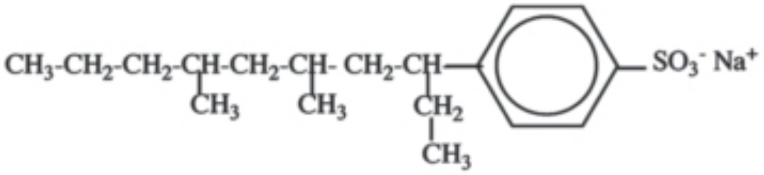
The detergent industries depend mainly on the aromatic sulphonic acid compounds after the treatment with caustic soda to obtain the water soluble sodium salt .



(detergent)

The molecule of detergent is composed of two parts (tail), it is a long carbon chain which is hydrophobic and the other part (head), is an ionic group which is hydrophilic .





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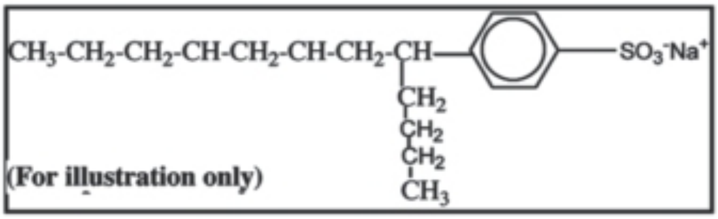
(Alky benzene sodium sulphonate ABS)(not biodegradable)



(For illustration only)

Linear alkylate – sodium sulphonate (LAS) (more biodegradable)

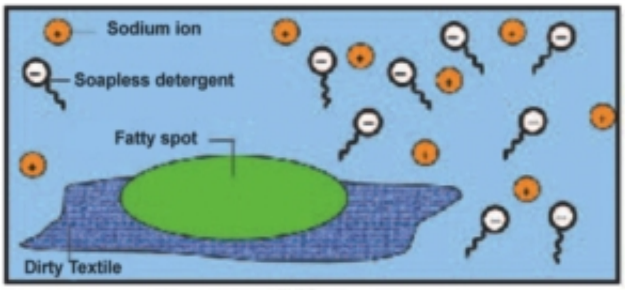
<u>How the detergents act :</u>

<u>How the detergentremoving the spots and dirties</u>.

Pure water doesn't remove dirties because grease which is saturated with dirties is insoluble in water because they are organic where water is polar compound, so soap less detergents are used.

This may be explain role of soap less detergent in remove the spots and dirties as follows:

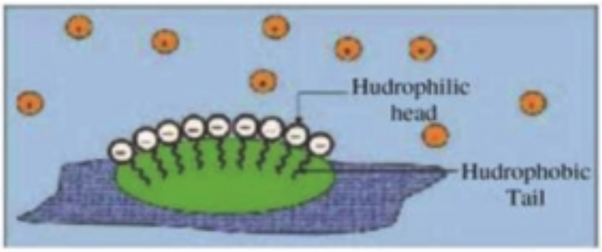
1- Adding detergent to water decrease the surface tension of water which increase ability of water to wet textile fig (5-8 A)



(A)

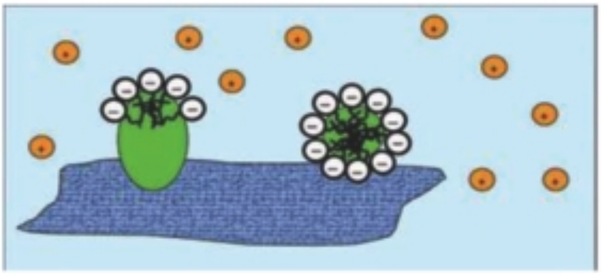
2- When the detergent is dissolved in water, their molecules arrange themselves where the hydrophobic tail of each molecule is directed towards the

dirties and adhere with them . While the hydrophilic head is directed towards water – so the detergent molecules surround the dirties completely The dirties completely covered by detergent molecule. fig (5-8 B)



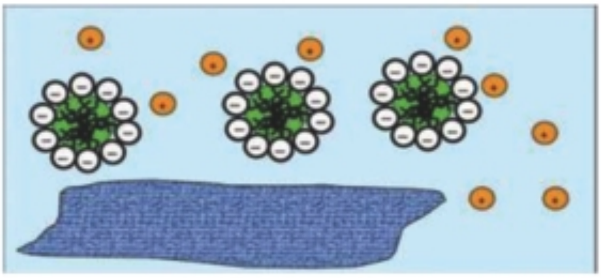
(B)

3- The frection produced from mechanical rubbing cause separation of the dirties and break them in to small balls fig (5-8 C)



(C)

4- The separation of small balls as result of repulsion force between heads of molecules {similar charges } and suspend in water in the form of emulsion which is removed by rinsing process as in fig (5-8-D)



(D)

The role of soap less detergents

Fig (5-8)

Hydrocarbons evaluation

1- Write the structural formula of the following compounds.

And write their correct name according to IUPAC system

a) 3 – pentene

b) 1,1 dimethy ethene

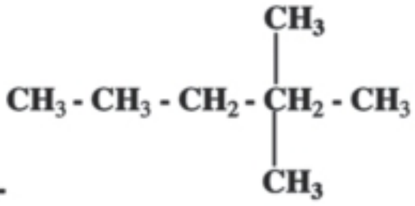
c) 3 – bromo propane

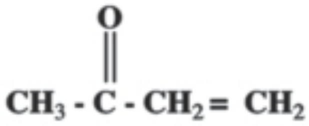
d) 2-ethy1-3-Methyl butane

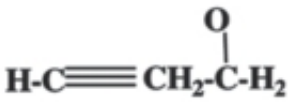
2-Which of the following formula represents alkanes , alkenes, alkynes or cycloalkanes.

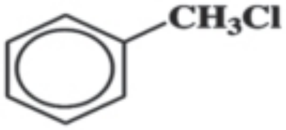
$C_{40}H_{82}$ - C_4H_{10} - C_6H_{12} - C_5H_{12} - C_3H_8

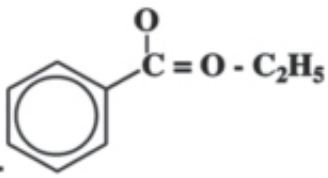
3-Write the following structural formula in a correct way.

a- 

b- 

c- 

d- 

e- 

4- Write the structural formula of the following compounds.

a) 3 – methyl - 1 – pentene

b) 4 – propyl - 2 – heptene

c) 4- methyl - 1- hexene

d) 1- chloro 2- phenyl ethane

e) 4- chloro – 4 Methyl – 2 - pentene.

5- Write the structural formula of the following hydrocarbons.

a- Open chain hydrocarbon contains six carbon atoms and two double bonds.

b- Open chain hydrocarbon contains six carbon atoms and three triple bonds.

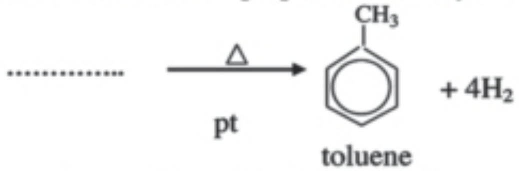
c- Open chain hydrocarbon contains five carbon atoms and one double bond.

dc- Cyclic hydrocarbon contains five carbon atoms and all its bonds are single .

6- Which of the following compounds represents an addition reaction :

1. $C_4H_8 + Cl_2 \longrightarrow C_4H_8Cl_2$
2. $C_7H_{16} \longrightarrow C_7H_8 + 4\ H_2$
3. $C_6H_6 + C_2H_5Cl \longrightarrow C_8H_{10} + H\ Cl$
4. $C_3H_6 + Cl_2 \longrightarrow C_3H_6Cl_2$

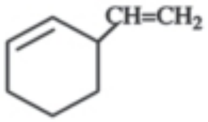
7- Benzene may be prepared from normal hexane when passed over a catalyst at high temperature by the catalytic reformation process. What is the name of the alkane which is used to prepare toluene by this methods.



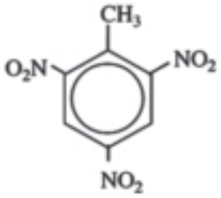
8- What are the number of hydrogen moles required to react with one mole of the following compounds to obtain saturated compounds

1- $CH_3 – CH = CH – CH = CH – CH_3$

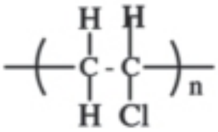
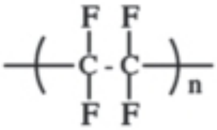
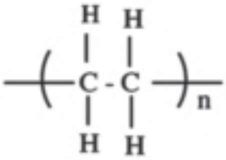
2-



9- What are the starting materials or chemicals required to prepare each of the following :

a-  b- c- d-

10- Draw the structural formula of the monomer required to prepare the following polymers.

 -  - 

11- Draw the first three repeated units of addition polymers for each of the following monomers :

- Ethene - 1, 2 dichloroethene 2- methyl - 1- propene

12- Write the name of the following compounds according to IUPAC system .

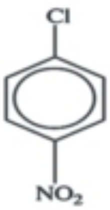
1- $CH_3 - CH_2 - CH_2 - CH_2 - C \equiv CH$

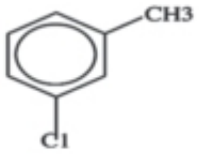
2- $CH_3 - CH_2 - \underset{|}{C}H - C \equiv CH$

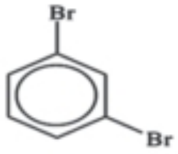
$CH_2 - CH_2 - CH_3$ (attached to the CH)

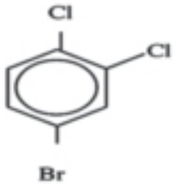
3- $CH_3 - C \equiv C - \underset{|}{C}H - CH_3$

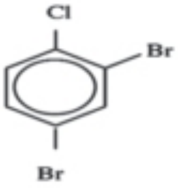
$CH_2 - CH_3$ (attached to the CH)

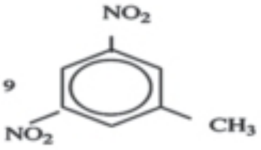
4 

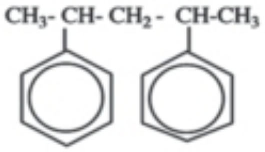
5 

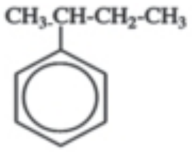
6 

7 

8 

9 

10 

11 

13- Give reason :

a- The organic compounds are abundant.

b- The structural formula is better than the molecular formula.

c- Alkanes are saturated compounds while alkenes are unsaturated compounds.

14- How can you identify the presence of carbon and hydrogen in organic compound.(with writing balanced equation).

15- How can you prepare methane gas in lab, draw the apparatus used then write the chemical equation.

16- Explain how ethene gas is prepared in lab. Draw the apparatus used and write the chemical equation.

17- Explain the effect of ethene gas on

1- Bromine water 2- potassium permanganate solution (in alkaline medium).

18- How can you obtain ethanal (acetaldehyde) from ethyne.

19- Explain the reaction of ethylene with each of the following:

Hydrogen – Bromine dissolved in carbon tetrachloride – hydrogen halide.

20- How benzene is prepared from sodium benzoate? write the chemical equation of the reaction.

21- Describe what happens in each of the following cases ,explaining the suitable conditions necessary to complete the reactions:

a- Hydrogenation of benzene in the presence of a catalyst.

b- Sulphonation of benzene.

c- Obtaining toluene from benzene.

22- Write the symbolic chemical equations represents each of the following reactions :

1- Addition reaction.
2- Addition polymerization reaction.
3- Elimination reaction.
4- Catalytic hydration reaction.
5- Thermal catalytic cracking reaction.
6- Oxidation reaction
7- Substitution reaction
8- Friedel craft's reaction.
9- Bayer's reaction.
10- Sulphonation reaction.
11- Nitration reaction.
12- Halogenations reaction.
13- Hydrogenation reaction.
14- Dehydration reaction.

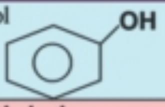
Hydrocarbon derivatives

Introduction :

In the past, classification of organic compounds was based on their physical properties like odour, taste and on some of their chemical properties. Due to the progress in the methods of chemical analysis it was found that the physical and the chemical properties of the compounds depends on the presences of certain groups known as functional groups .

The functional or the characteristic groups

It is a group of atoms combine together by a certain way, to form a part of the molecule. However, its activity affects properties of the whole molecule. Organic compounds were classified into groups; each one is characterized by a certain function group. The following table illustrates the classes of the organic compounds and their functional group :

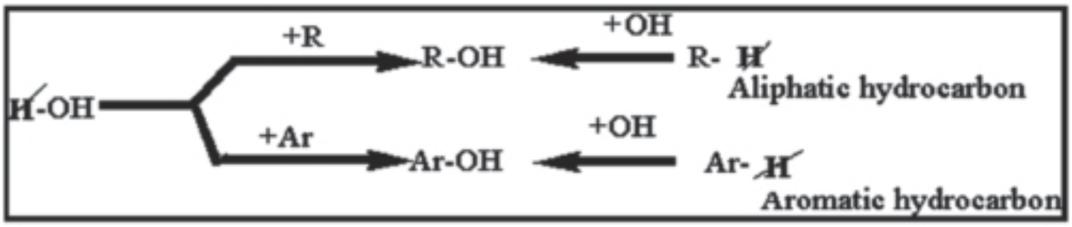
The class	General formula	The functional group	example
Alcohols	R – OH	The hydroxyl – OH	Methyl alcohol CH_3OH
Phenols	Ar – OH	The hydroxyl –OH	Phenol 
Ethers	R – O – R	Etherial – O –	Dimethyl ether $CH_3 - O - CH_3$
Aldehydes	R – CHO	Formyl $-\overset{H}{\overset{\mid}{C}}=O$	Acetaldehyde $CH_3 - CHO$
Ketones	$R-\overset{O}{\overset{\parallel}{C}}-R$	Carbonyl – C = O	Acetone $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$
Carboxylic acids	$R-\overset{O}{\overset{\parallel}{C}}-OH$	Carboxylic – COOH	Acetic acid CH_3COOH
Esters	$R-\overset{O}{\overset{\parallel}{C}}-OR$	Ester – COOR	Ethyl acetate ester $CH_3COOC_2H_5$
Amines	$R - NH_2$	Amino $- NH_2$	Ethyl amine $C_2H_5NH_2$

Alcohols and phenols

Alcohols and phenols are organic compounds their molecules contain one or more hydroxyl group. If it is attached to an alkyl group (R) the compound is called alcohol, whereas, if it was attached to an Aryl group (Ar) the compound is called phenol.

Ar - OH **Phenol**	**R - OH** **Alcohol**
Phenol	CH_3 - OH Methyl alcohol

Alcohols and phenols are considered as alkyl or aryl derivatives of water by replacing one hydrogen atom in water molecule by an alkyl or aryl group. They may also be considered as hydroxyl derivatives of the aliphatic or aromatic hydrocarbons by replacing one or more hydrogen atom by one or more hydroxyl group.



1-Alcohols

Nomenclature of alcohols:

There are two methods

a- According to the alkyl group (Common nomenclature):

In this methods the alcohol is named according to the name of alkyl group present in the alcohol molecule. The word alcohol is added to the name of the alkyl group e.g methyl alcohol CH_3OH, ethyl alcohol C_2H_5OH.

b- The nomenclature according to IUPAC :

The name of alcohol is derived from the name of the corresponding alkane (which contains the same number of carbon atoms) then adding the suffix "ol" instead of "e" like CH_3OH methanol, C_2H_5OH ethanol. In this system the carbon chain is numbered from the nearest end to the hydroxyl group.

From pentane we can derive 3 different isomeric alcohols.

1- $CH_3-CH_2-CH_2-CH_2-CH_2OH$ — 1- Pentanol

2- $CH_3-CH_2-CH_2-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_3$ — 2- Pentanol

3- $CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_2-CH_3$ — 3- Pentanol

N.B. In case of common nomenclature the name "iso" is used if the carbon atom of (- OH) group is attached to two carbon atoms .

$CH_3-CH_2-CH_2-OH$	$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-OH$
Normal propyl alcohol	iso propyl alcohol
or 1- propanol	or 2 - propanol

Exercise:

1- Write the common name and the IUPAC of the following alcohols

$CH_3-\underset{OH}{\underset{|}{C}}H-CH_3$ $\qquad$ $CH_3-CH_2-\underset{OH}{\underset{|}{C}}H-CH_3$

2- Write structural formula of the following alcohols:

isopentyl alcohol $\qquad$ 2,2- dimethyl -1- butanol

Classification of alcohols.

Alcohols are classified according to the number of hydroxyl groups in the alcohol molecule into four types, these are:

Monohydric	Dihydric	Trihydric	Polyhydric
CH_3OH	**$C_2H_4(OH)_2$**	**$C_3H_5(OH)_3$**	$C_6H_5(OH)_6$
Methanol	$\underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH_2}}$	$\underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{CH_2}}$	$\underset{OH}{\underset{\vert}{CH_2}}-(CHOH)_4-\underset{OH}{\underset{\vert}{CH_2}}$
	Ethylene glycol (1,2 dihydroxy ethane)	Glycerol (1,2,3 tyi hydoxy propane)	Sorbitol

Monohydric alcohols are classified into three kinds according to the type of carbinol group (carbon atom attached to the hydroxyl group).

Classification of alcohols according to carbinol

Primary alcohols	Secondary alcohols	Tertiary alcohols
Carbinol group attached to one carbon atom and two hydrogen atoms.	Carbinol group attached to two carbon atoms and one hydrogen atom.	Carbinol group attached to three carbon atoms.
$CH_3-C(H)(H)-OH$	$CH_3-C(H)(CH_3)-OH$	$CH_3-C(CH_3)(CH_3)-OH$
Ethyl alcohol (ethanol)	2-propanol (Isopropyl alcohol) Secondary propanol	2-methyl-2-propanol tertiary butyl alcohol

Exercise:

What is the type of the following alcohols:

1- $CH_3-CH_2-CH(OH)-CH_3$ Monohydric secondary alcohol

2- $C_2H_4(OH)_2$ Dihydric alcohol

3- $(CH_3)_2CH-CH_2-OH$ Monohydric primary alcohol

4- $C_6H_8(OH)_6$ polyhydric alcohol

5- $CH_3-CH_2-C(CH_3)_2-OH$ Monohydric tertiary alcohol

Monohydric Primary Alcohols

Ex: Ethyl alcohol (ethanol)

C_2H_5OH

Ethanol is considered as the oldest organic compound prepared in industry. Ancient Egyptians prepared alcohol since 3 thousand years ago by the fermentation of sugar and starch materials.

Methods of preparation of ethanol (in industry)

1- **By alcoholic fermentation:**

20% of ethanol is produced all over the world by alcoholic fermentation process of starch and sugar materials specially in countries which are rich in the cultivating sugar- cane, beet and maize. In Egypt ethanol is prepared from molasses (sucrose) (in the Egyptian sugar, distillation company in Howamdeia). The fermentation process takes place by the addition of yeast to molasses (sucrose) where ethanol and carbon dioxide gas are formed as follows:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}{}_{(s)} + H_2O_{(l)} \xrightarrow[H^+]{\text{hydrolysis}} \underset{\text{glucose}}{C_6H_{12}O_6}{}_{(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6}{}_{(aq)}$$

$$C_6H_{12}O_6{}_{(aq)} \xrightarrow[\text{zymase enzyme}]{\text{yeast}} \underset{\text{ethanol}}{2C_2H_5OH}{}_{(l)} + 2CO_{2(g)}$$

2- By catalytic hydration of ethene

It is the common method for preparation of ethanol. It is carried out in most of the petroleum countries. Thermal cracking of long chain petroleum materials ethene is obtained. Then by catalytic hydration of ethene with diluted sulphuric or phosphoric acid ethanol is obtained.

$$\text{Petroleum product} \xrightarrow{\text{cracking}} CH_2{=}CH_{2(g)} + H_2O_{(l)} \xrightarrow[110^0C]{H_2SO_4} C_2H_5OH_{(l)}$$

Therefore, ethanol is considered as a petrochemical compound (chemicals that produced from petroleum).

N.B. Ethene is the only alkene which gives primary alcohol by catalytic hydration, while the other alkenes give secondary or tertiary alcohols (Markownikoff's rule)

$$\underset{\text{propene}}{CH_3\text{-}CH{=}CH_{2\,(l)}} + H_2O_{(l)} \xrightarrow{H_2SO_4} \underset{\text{2-propanol(Sec.alcohol)}}{CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{C}}H\text{-}CH_{3\,(l)}}$$

$$\underset{\text{2 - Methyl-2-butene}}{CH_3\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH\text{-}CH_{3\,(l)}} + H_2O_{(l)} \xrightarrow[110^0C]{H_2SO_4} \underset{\text{2-Methyl-2-butanol[Tert.alcohol]}}{CH_3\text{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}\text{-}CH_2\text{-}CH_{3\,(l)}}$$

<u>**The converted alcohol:**</u> **(red spirit)**

Pure ethanol of 96% concentration is expensive because of the high production tax which should be paid for it. This is imposed to minimize its use in making alcoholic liquors because of their harmful effect on health and social aspects. However, ethanol is very important as fuel, in the chemical industries and organic solvent. Some additives are added to ethanol to be used as fuel with low price. These poisonous additives like methanol (causes madness and blindness) , pyridine (with bad odour) and coloured dyes. These additives cannot be easily separated from alcohol except with very complicated chemical processes besides, it is illegal.

<u>**The general method of Preparation of alcohols:**</u>

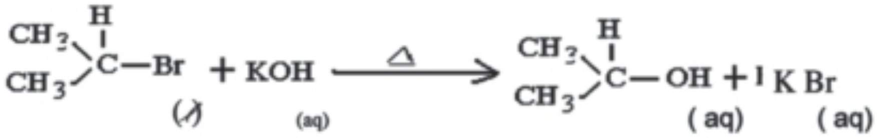
By heating alkyl halides (RX) with aqueous solution of strong alkalies, where the halide radical is replaced by hydroxyl group and the corresponding alcohol is formed.

$$RX + KOH_{(aq)} \xrightarrow{\Delta} R-OH + KX$$

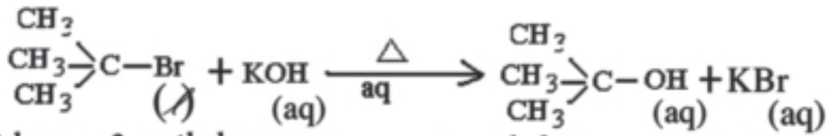
where R = the alkyl radical , X = halide radical.

Ex:

$$\underset{\text{Ethyl bromide}}{CH_3\text{-}CH_2\text{-}Br_{(l)}} + KOH_{(aq)} \xrightarrow{\Delta} \underset{\text{Ethanol(primary alchol)}}{CH_3\text{-}CH_2\text{-}OH_{(aq)}} + K\,Br_{(aq)}$$



2. bromo propane **2-propanol (Secondary alcohol)**



2-bromo-2-methyl.propane 2-methyl-2-propanol (Tertiary alcohol)

N.B. Halides may be arranged in the following sequence according to the ease of displacement. Chlorides < bromides < iodides

Therfore alkyl Iodide is the most easy to by hydrolised

<u>Exercise</u> :

What is the suitable alkyl halide to be used to prepare the following alcohols (Write the chemical equation) 1) Methanol 2) 2- butanol

3) 2- Methyl 2- pentanol

General properties of alcohols

The physical properties:

Alcohols are neutral colourless compounds. The first members are light liquids completely miscible with water. The mild members are oily, however, the higher ones are solid waxes.

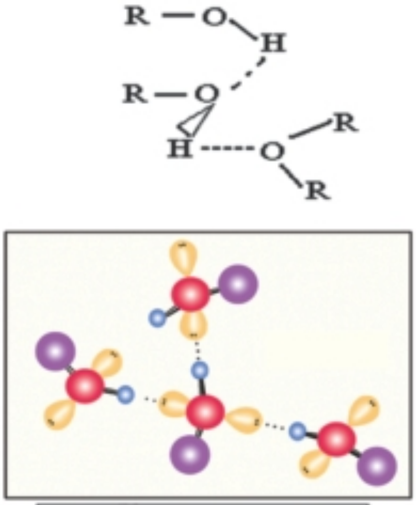
Alcohols especially the first members are completely soluble in water and their boiling points are relatively high .These properties are different from those of alkanes.

Alcohol	Boiling point
C_2H_5OH ethanol	78˚C
$C_2H_4(OH)_2$ ethylene glycol	197˚C
$C_3H_4(OH)_3$ glycerol	290˚C

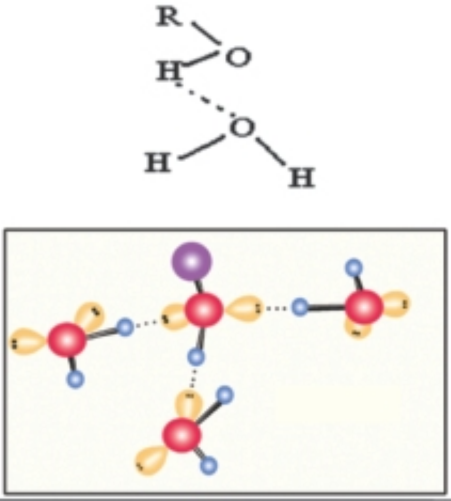
The solubility in water and the high boiling points of alcohols are attributed to the presence of the polar hydroxyl groups which have the ability of forming hydrogen bonds either between the alcohol molecules themselves fig (5 -9)

or between the alcohol molecules and the water molecules fig (5- 10)

. As the number of hydroxyl groups increases in the alcohol molecule , we observe the increases of its solubility in water , beside the increase of its boiling point .



Hydrogen bonds between alcohol molecules .
fig (5 -9)



Hydrogen bonds between alcohol molecules and water molecules .
fig (5- 10)

<u>**Chemical properties**</u> :

The chemical properties of alcohols may be classified as follows :

1- Reactions specific to hydrogen of the hydroxyl group.

2- Reactions specific to the hydroxyl group.

3- Reactions specific to the carbinol group.

4- Reactions specific to the whole molecule.

1- <u>Reaction specific to the hydrogen of the hydroxyl group</u>.

a- <u>Acidity of alcohols .</u>

We have mentioned that alcohols have neutral effect on litmus, but a weak acidic character may appear specially when it reacts with strong active metals e.g sodium or potassium which can replace the hydrogen of the hydroxyl group.

$$2\,R - OH + 2\,K \rightarrow 2\,ROK_{\text{ potassium alkoxide}} + H_2$$

The weak acidic property of alcohol is related to the presence of the polar covalent bond which combine the hydrogen atom to oxygen atom in the hydroxyl group .The electron pair is shifted towards the oxygen atom, this facilitate the breakdown of the polar covalent bond so the metal atom can replace the hydrogen of the hydroxyl group .

$$\underset{(l)}{2C_2H_5OH} + \underset{(s)}{2Na} \longrightarrow \underset{\text{sodium ethoxide}\,(l)}{2C_2H_5ONa} + \underset{(g)}{2H_2} \uparrow_{\text{burns with pop sound}}$$

Exercise :

Write the chemical equation for the reaction of sodium with methanol.

Practical experiment:

Place 5 ml of ethanol in a test tube then add a small piece of sodium metal. Cover the tube opening with your thumb to keep the evolving gas. Observe the effervescence and evolution of hydrogen gas which burns with a pop. After the reaction is completed evaporate the solution on water bath and observe the formation of a white solid substance which is sodium ethoxide. The ethoxide may be hydrolyzed giving ethanol and sodium hydroxide .

$$C_2H_5ONa_{(l)} + H_2O_{(l)} \longrightarrow C_2H_5OH_{(aq)} + NaOH_{(aq)}$$

b- **Ester formation :**

Alcohols react with organic acids to form esters. In this reaction hydrogen atom is separated from the hydroxyl group of alcohol molecule and a hydroxyl group is separated from the acid. This was proved by reacting alcohol containing the heavy oxygen isotope O^{18}, with acetic acid containing the normal oxygen isotope O^{16} by analyzing the oxygen of the formed water, it was found that it is of the normal isotope.

$$CH_3CO^{16}O^{16}H + C_2H_5O^{18}H \xrightarrow{H_2SO_4} CH_3COOC_2H_{5(aq)} + H_2O^{16}_{(l)}$$

Ester formation reaction is a reversible reaction therefore concentrated sulphuric acid should be added to prevent the reversible reaction, (we will study esters in details later)

2- **Reactions specific to the hydroxyl group.**

Because alcohols contain a hydroxyl group, therefore, they react with halogenated acid (HX).

eg.: Ethanol reacts with conc. hydrochloric acid in the presence of zinc chloride as a catalyst to form ethyl chloride.

$$C_2H_5OH_{(\ell)} + HCl_{(aq)} \xrightarrow[\text{catalyst}]{ZnCl_2} C_2H_5Cl_{(aq)} + H_2O_{(\ell)}$$

Exercise : **How do you obtain ethanol from ethyl chloride and vice versa.**

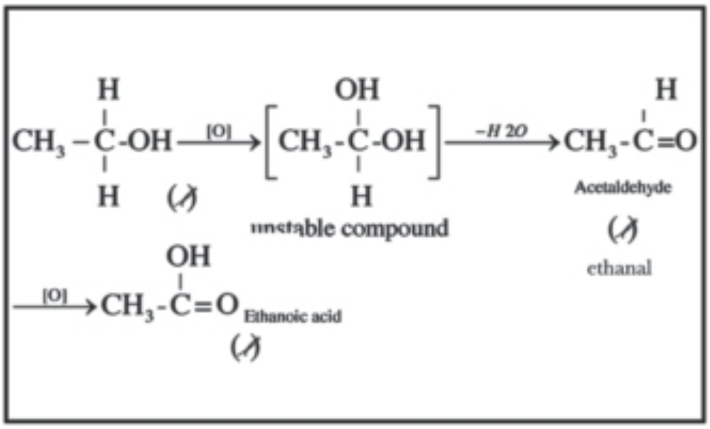
3-Reactions specific to carbinol group : $-\overset{|}{\underset{|}{C}}-OH$

Alcohols are easily oxidized by oxidizing agent e.g. acidified potassium dichromate or potassium permanganate, the products differ according to the type of alcohol.

The action of oxidizing agents is concerned with the hydrogen atoms attached to the carbinol, converting them to hydroxyl groups. We must put into consideration that when two hydroxyl groups are attached to the same carbon atom, the produced compound is unstable and instanteously loses a water molecule and converted to a stable compound.

a- primary alcohols :

The two hydrogen atoms attached to the carbinol are oxidized in two steps. In the 1st step the aldehyde is produced, then the acid is produced in the second step. For instance, ethanol is oxidized by hot chromic acid to acetaldehyde then to ethanoic acid.



Practical experiment :

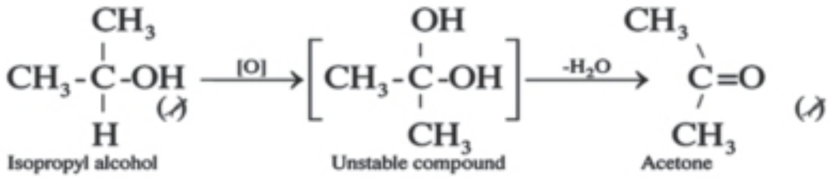
Put three ml of ethanol in a dry clean test tube. Add the same amount of acidified potassium dichromate. Heat the mixture in a water bath for 10 minutes. We observe that the colour of the solution changed from orange to green colour. The odour of vinegar (ethanoic acid) appears.

If we use acidified potassium permanganate as oxidizing agent we notice the disappearance of its violet colour.

This reaction is used to detect the taking of drivers for liquors , where it can be allowed to blow a balloon through a tube containing silica gel saturated with acidified potassium dichromate . The balloon is left till the exhalation goes out. If the deriver was drunk the colour of potassium dichromate in the tube changed from orange to green colour.

b- Oxidation of secondary alcohols:

The single hydrogen atom attached to the carbinol group is oxidized in one step by the previous method, where ketone is formed. For example isopropyl alchol is oxidized to acetone (propanone).



c- Oxidation of tertiary alcohols:

Since carbinol group is not attached with any hydrogen atoms, it is difficult to be oxidized under these conditions.

4- Reaction specific to the whole molecule:

Alcohols react with concentrated sulphuric acid and the reaction product depends on number of alcohol molecules as well as temperature. When they are heated to 180^0c, a water molecule is eliminated from one alcohol molecule giving alkene.

$$\begin{array}{c} \text{H}\ \text{H} \\ \text{H-}\overset{|}{\underset{|}{\text{C}}}\text{-}\overset{|}{\underset{|}{\text{C}}}\text{-OH}_{(l)} \\ \text{H}\ \text{H} \end{array} \xrightarrow{H_2SO_4 - (180^0c)} H_2C{=}CH_{2(g)} + H_2O_{(v)}$$

N.B :

If the temperature is 140°C, the conc. sulphuric acid eliminate one molecule of water from every two molecules of the alcohol giving ether.

$$\begin{array}{l} C_2H_5OH \\ C_2H_5OH_{(l)} \end{array} \xrightarrow[140^0C]{H_2SO_4\ conc.} \underset{diethylether\ (g)}{C_2H_5\text{-}O\text{-}C_2H_5} + H_2O_{(l)}$$

<u>The economical important of alcohol (uses of alcohol):</u>

1- They are used as solvents for organic compounds as oils and fats and used in chemical industries e.g. preparation of drugs , paints and polishes.

2- Ethanol is used in sterilizing mouth and teeth also it is used as disinfectant which has a great effect on killing microbes.

3- Ethanol is used in the manufacture of perfumes and alcoholic liquors. We must put into consideration the bad effect of alcoholic drinks for man's heath , like the liver fibrosis , cancer of stomach and oesophagus.

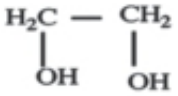
4- It may be mixed with gasoline which is used as a fuel. In some countries, such as Brazil.

5- It is the main component of converted alcohol (85% ethanol + 5% methanol + 1% another additive + colour, odour and the rest is water) .

5- Ethanol freezes at (-110°C) so it is used to fill special thermometers which measure the lower temperature until (- 50°C) as it has low freezing point (-110.5°c).

2- Dihydric alcohols :

e.g:



Ethylene glycol
(1,2 dihydroxy ehane)

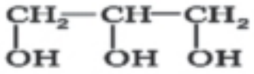
1- It is used as antifreeze substance in car radiators in cold countries.

2- Due to its high viscosity it is used as a constituent of the liquids used in the hydraulic break in addition it is used in printing ink .

3- It is used to prepare polyethylene glycol (PEG) which is used in the manufacture of Dacron fibers, photographic films and cassette tapes.

3- Trihydric alcohols .

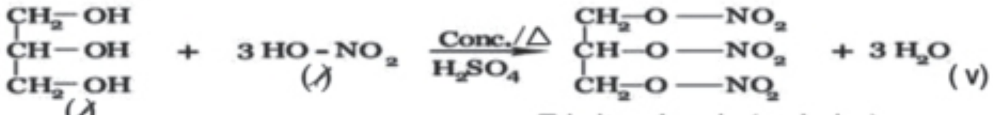
Glycerol (1,2,3 trihydroxy propane)



1- It is used in the manufacture of creams and cosmetics as a moisturizer of skin.

2- It is used in the manufacture of textiles, since it renders them soft and flexible.

3- It is used in the preparation of explosive substance nitroglycerine obtained by nitration of glycerin by a mixture of concentrated, nitric and sulphuric acids.

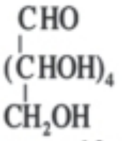


Tri nitro glycerin (explosive)

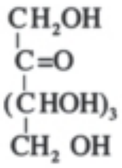
* Nitroglycerine is also used to widen arteries in the treatment of heart problem.

4- Polyhydric alcohols

Carbohydrates are considered as polyhydroxy aldehydic or ketonic substances. Their molecules contain more than one hydroxyl group in addition to aldehydic or ketonic group as example glucose or fructose $C_6H_{12}O_6$.



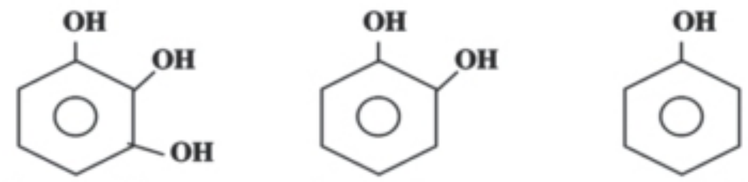
condensed structural formula of glucose



condesed Structural formula of fractose

Phenols

Phenols are hydroxy aromatic compounds where one or more hydroxyl group are directly attached to the carbon atoms of the benzene ring.



Pyrogallol (1.2.3 trihydroxy Benzene) | **Catechol (1.2.dihydroxy Benzene)** | **Phenol (Hydroxyl Benzene)**

We will study phenol in details as an example of this group.

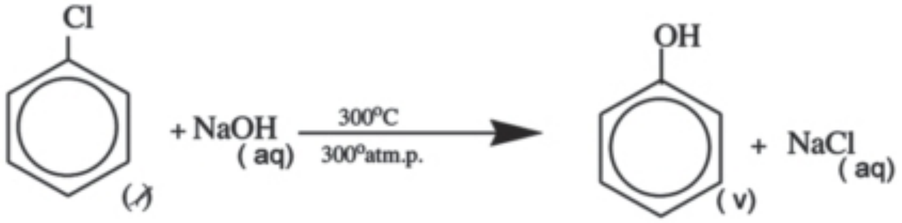
-Phenol (carbolic acid) C_6H_5OH:

Phenol is an organic compound which has a great industrial importance. It is used as a starting material for many industrial products e.g polymers, dyes, disinfectants, salicylic acid derivatives (as aspirin) and picric acid.

Preparation of phenol.

1- From fractional distillation of coal tar.

2- From halogenated aromatic compounds, by the hydrolysis of chlorobenzene with sodium hydroxide at high temperature and high pressure 300 atmospheres.



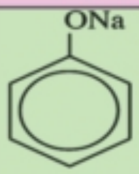
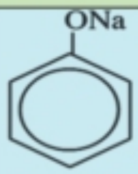
Physical properties :

Phenol is a solid corrosive substance. It has a characteristic odour, melts at 43°C. Phenol is sparingly soluble in water, its solubility in water increases by raising the temperature, it becomes completely miscible with water at 65°C.

Chemical properties :

1- Acidity of phenol compared to alcohols:

It is known that the acidic properties are attributed to the presence of hydrogen ion. It is clear from the following table that alcohols and phenol react with strong metals like sodium and hydrogen gas is evolved. This is due to the polarity of (O-H) bond this polarity increases in the case of phenol due to the presence of benzene ring in phenol. The increasing in the polarity of hydroxyl group means the increase in the bond length in (O-H) and its weakness , which facilitate the separation of hydrogen ion . That is why phenol reacts with alkalis such as caustic soda , and considered as an acid named in industry by **carbolic acid** .

Points of comparison	R-OH alcohol	phenol
Reaction with sodium metal	R-ONa+H_2	 + H_2
Reaction with sodium hydroxide	No reaction	 + H_2O

2- Rection of phenol with halogen acids compared to alcohols:

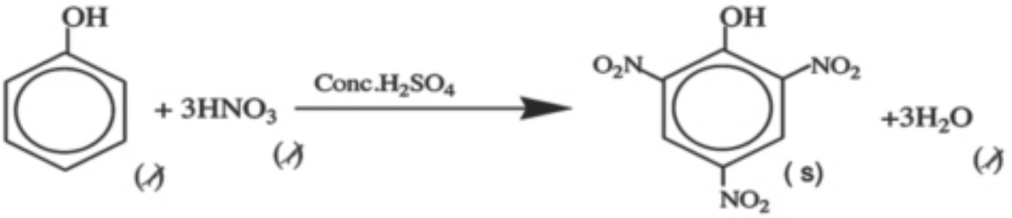
Benzene ring also affects the bond between the carbon atoms of benzene ring in phenol and the oxygen atom of the hydroxyl group, this makes the bond more shorter and more strong .

So it is impossible to eliminate the hydroxyl group from phenol when it reacts with acids , while alcohols react easily with acids.

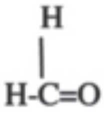
Point of comparison	R-OH Alcohol	OH phenol
Reaction with HCl	$RCl + H_2O$	Do not react due to the strong bond between oxygen and benzene ring.

3- Nitration of phenol :

Phenol reacts with concentrated nitric acid to form tri-nitrophenol which is known commercially as picric acid. It is used in the manufacture of explosives and treatment of burns. It gives the skin a yellow colour, which is difficult to be removed and it remains for several days until the skin (outer layer) renewed.



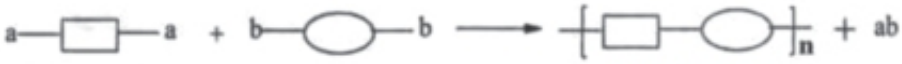
Trinitrophenol(Picric acid)

4- With formaldehyde : 

Phenol reacts with formaldehyde in acidic or alkaline medium to form copolymer, then polymerization process takes place by condensation to form bakelite polymer.

Polymerization by condensation.

These are copolymers produce usually from the combination of two types of monomers , with the elimination of a small molecule e.g water molecule.



Copolymer

The first step begins by the reaction between a molecule of formaldehyde with two molecules of phenol where H_2O molecule is produced. Then the molecules of copolymer combine together in sequence to form a network polymer called Bakelite.

Bakelite is a type of thermosetting plastic which is heat resistant, which is important as a good electrical insulator. Therefore, it used in the manufacture of some electric instruments and ash trays. Bakelite has a dark brown colour.

Detection of phenol.

1- On adding few drops of iron III chloride solution to phenol, a violet colour is produced.

2- On adding bromine water to phenol, a white precipitate is produced.

Questions on alcohols and phenols

QUESTION 1:-

Write short note on each of the following :

a- Acidity of alcohols and phenols.

b- Converted alcohol.

c- Ester formation reaction.

d- Uses of ethanol.

e- Trinitro glycerin .

f- Picric acid.

QUESTION 2 :-

Choose from column (B) what is suitable for column (A):

No.	A	B
1	Trihydric alcohol	1- Pyrogollol
2	Tertiary alcohol	2- Sorbitol
3	Dihydric alcohol	3- Phenol
4	Secondary alcohol	4- Picric acid
5	1,2,3- tri hydroxyl benzene	5- glycerol
6	Carbolic acid	6- Iso propyl alcohol
7	tri nitro phenol	7- ethylene glycol.
		8- 2-Methyl-2- ropanol

QUESTION 3 :-

How can you carry out the following experiments – explain your answer by chemical equations.

a- Oxidation of ethanol.

b- Preparation of sodium ethoxide.

QUESTION 4 :-

What the effect of the following on ethanol.

a- Sodium metal

b- Hydrogen chloride

c- Hot chromic acid .

d- Concentrated sulphuric acid

QUESTION 5 :-

What is the effect of the following on phenol :

a- Sodium metal.

b- Caustic soda.

c- Concentrated nitric acid and concentrated sulphuric acid.

d- Formaldehyde

QUESTION 6 :-

How can you carry out the following conversions - Explain the conditions of each reaction :

a- Ethanol from long chain petroleum products.

b- Ethyl bromide from ethanol and vice-versa.

c- Ethanol from ethylene and vice versa.

d- Acetone from iso propyl alcohol.

e- Phenol from chlorobenzene

f- Phenol from benzene and vice -versa.

QUESTION 7 :-

Write the structural formula of each of the following compounds:

1) 2- ethyl- 1- propanol   2) 2- Methyl - 3- butanol

3) 3- Ethyl -2- butanol   4) 1 , 1- dimethyl - 1- butanol

QUESTION 8 :-

Arrange the following in ascending order according to their boiling points – Giving reasons:

glycerol – ethanol – ethylene glycol – sorbitol.

QUESTION 9 :-

1- CH_3-CH_2-OH	2- $CH_3-CH_2-CH_2-OH$
3- $CH_3-CH-OH$ $\quad\quad\quad\ \ CH_3$	4- $CH_2-CH-OH$ $CH_3\ \ CH_3$
5- $CH_3-CH-CH_2-OH$ $\quad\quad\quad\ \ CH_3$	$\quad\quad\quad\ \ CH_3$ 6- CH_3-C-OH $\quad\quad\quad\ \ CH_3$

Choose from the previous table the correct answer for each of the following questions.

1- Secondary alcohols

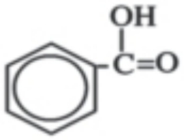
2- Compound that does not oxidize by normal oxidizing agents.

3- The compounds which oxidized to ketones.

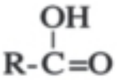
4- The compounds which produce ether when react with concentrated sulphuric acid at 140°C.

Carboxylic acid

Carboxylic acids are considered the most acidic organic compounds. However , they are not strong acids like the inorganic acids e.g hydrochloric, sulphuric, nitric acids. Carboxylic acids form a homologous series which are characterized by the presence of one or more carboxylic group (-COOH). The carboxylic group may be attached to an alkyl radical to give an aliphatic acid , or attached directly to a benzene ring and give aromatic acids.

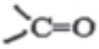


Aromatic acid



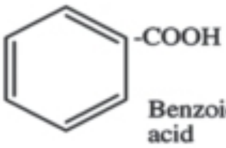
Aliphatic acid

The saturated monocarboxylic aliphatic acids are named fatty acids because many of them are present in fats in the form of ester with glycerol.

The carboxylic group (-COOH) is the functional group of organic acids . It is composed of two groups i.e. the carbonyl group and the  hydroxyl group (-OH).

<u>Types of carboxylic acids:</u>

A) Monocarboxylic acids (Monobasic)

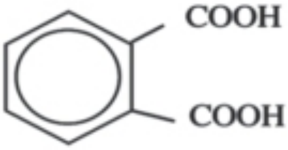


Benzoic acid

HCOOH Formic acd

B) Diccarboxylic acids (Dibasic acids)

Oxalic acid



Phthalic acid

Nomenclature of carboxylic acids

The common names

The carboxylic acids are usually named by common names which are derived from the Latin name of the source from which the acid is prepared. For example formic acid is derived from ants (Formica) because the acid was prepared for the first time from the distillation of crushed ants. Acetic acid is derived from vinegar (Acetum) and butyric acid is derived from (Butyrum) and palmetic acid is derived from (Palm oil).

IUPAC nomenclature :

The common name of acids are more used than the other common names of organic compounds . In the (IUPAC) nomenclature of acids , the name of the acid is derived from the name of the corresponding Alkane that contains the same number of carbon atoms by adding the suffix (oic) to the name of alkane instead of the letter (e).

The following table shows the common and the (IUPAC) names of some carboxylic acids.

Formula	Common name	Corresponding alkane	IUPAC
HCOOH	Formic acid Ants Ant (Formica)	Methane	Methanoic acid
CH_3 COOH	Acetic acid Vinegar (Acetum)	Ethane	Ethanoic acid
C_3 H_7 COOH	Butyric acid Butter (Butyrum)	Butane	Butanoic acid
$C_{15}H_{31}$ – COOH	Palmetic acid (Palm oil)	Hexadecane (Contain16 carbon atoms)	Hexadecanoic acid

We shall study acetic acid as an example of the monocarboxylic aliphatic acids, we will know the method of its preparation in industry.

The methods of preparation of acetic acid in industry:

1- Biological method:

Acetic acid (Vinegar) is prepared in (Egypt) by the oxidation of diluted alcoholic solutions by atmospheric oxygen in the presence of a special type of bacteria known as vinegar bacteria.

2- Preparation from acetylene:

Acetic acid is prepared in industry on a large scale by catalytic hydration of acetylene where acetaldehyde is produced, which is easily oxidized to the acid.

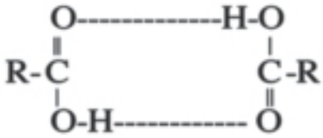
$$\underset{(g)}{H\text{-}C\equiv C\text{-}H} + \underset{(l)}{H_2O} \xrightarrow[HgSO_4\ /60^0C]{H_2SO_4\ (40\%)} \underset{(l)}{CH_3\text{-}\overset{\overset{\large H}{|}}{C}=O} \xrightarrow{[O]} \underset{(l)}{CH_3\text{-}\overset{\overset{\large OH}{|}}{C}=O}$$

General properties of aliphatic acids:

Physical properties :

The physical properties of organic acids are graduated by increasing their molecular masses. The first four members are corrosive liquids to skin and posses pungent irritating odour. They are completely miscible with water. The successive members are oily liquids and have an unpleasant odour and sparingly soluble in water. As the molecular mass of the acids increase they become solids, odourless and insoluble in water.

By comparing the boiling points of carboxylic acids with those of alcohols which have the same number of carbon atoms , we find that the boiling point of acids are higher . This is attributed to the association of molecules by hydrogen bonds. Each acid molecule is linked to another molecule by two hydrogen bonds .



Acid	Molecular mass	b.p °C	Alcohol	Molecular mass	b.p° C
Formic	46	100	Ethanol	46	78
Acetic	60	118	Propanol	60	98

Chemical properties

1- Reactions attributed to the hydrogen ion :

*** Acidity and salt formation :**

The acidic property of carboxylic acids appears in their reactions with metals preceed hydrogen in the electrochemical series, oxides , hydroxide and carbonate , bicarbonate salts to form organic salts.

$$2\ CH_3COOH_{(aq)} + Mg_{(s)} \longrightarrow \underset{\text{Magnesium acetate}}{(CH_3COO)_2Mg_{(aq)}} + H_{2\,(g)}$$

$$CH_3COOH_{(aq)} + NaHCO_{3(s)} \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa_{(aq)}} + H_2O_{(\ell)} + CO_{2(g)}$$

We notice that all carboxylic acids are weak acids , their strength are much lower than inorganic acids.

2- Reactions attributed to hydroxyl group

*** Ester formation**

Organic acids reacts with alcohols to form ester and water.

$$R-\overset{\overset{O}{\|}}{C}=OH + H-OR \xrightarrow[Conc.]{H_2SO_4} R-\overset{\overset{OR}{|}}{C}=O + H_2O$$

3- Reactions attributed to the carboxylic group :

Carboxylic acids are reduced by hydrogen in the presence of copper chromate $CuCrO_4$ at 200°C as a catalyst. Ethanol may be prepared from acetic acid by this method. This reaction is opposite to that of oxidation of alcohols to acids.

$$CH_3-\overset{\overset{O}{\|}}{C}-OH_{(aq)} + 2H_{2\,(g)} \xrightarrow[200^0c]{CuCrO_4} CH_3-CH_2-OH_{(v)} + H_2O_{(v)}$$

Detection of acetic acid :

1- Acidity test :

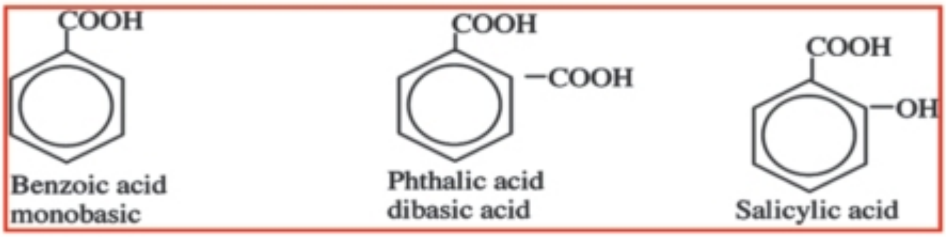
when the acid is added to sodium carbonate or bicarbonate effervescence takes place and CO_2 gas is evolved which turbid lime water.

2- Ester formation test :

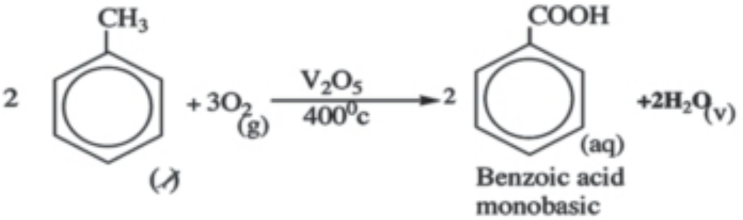
Acids react with alcohols to form esters which are characterized by a pleasant odour and they are responsible for the odour and flavour of most of fruits and flower according to the kind of alcohol and acid.

Aromatic Carboxylic acids

Aromatic carboxylic acids are compounds containing one or more carboxylic group attached directly to a benzene ring. Benzoic acid is an example of monocarboxylic (monobasic acid) aromatic acids and phthalic acid is an example of dicarboxylic (dibasic) aromatic acids .

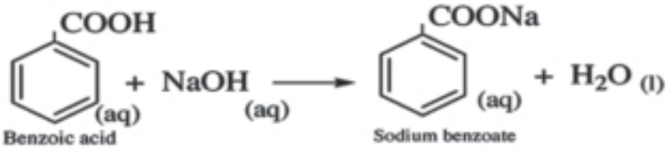


Benzoic acid can be prepared commercially by the oxidation of toluene by the proper oxidizing agent. It is prepared commercially by the oxidation of toulene in atmospheric air at 400°C and in the presence of vanadium pentoxide V_2O_5.



Aromatic acids are generally stronger, less soluble in water and less volatile than aliphatic acids. The reaction of the carboxylic group resembles that of

aliphatic acids. This can be represented by the formation of salts with metals, their hydroxides or carbonates and the formation of esters with alcohols.



The organic acids in our life

1- Formic acid(HCOOH):-

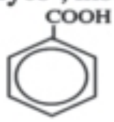
It is the acid which is secreted by ants to defend themselves. It is used in the manufacture of dyes , insecticides, perfumes, drugs and plastics.

2- Acetic acid CH_3COOH (pure 100%):

It is colourless, corrosive to skin and has pungent odour. It freezes at 16°C forming solid substances as ice .Therefore it is called glacial acetic acid. Acetic acid 4% is used as vinegar in homes . It is considered as a starting material for the synthesis of many organic products .

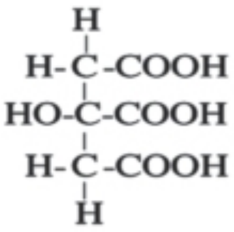
e.g. synthetic silk, dyes , insecticides and food additives.

3-Benzoic acid:



It is sparingly soluble in water .It is converted to its sodium or potassium salts to become soluble in water and easily absorbed in the human body . Sodium benzoate 0.1% is used as foods preservating substance, because it prevents the growth of fungi on foods.

4- Citric acid:



It is found in fruits its percent is 5 – 7 % in lemon and 1 % in orange , It prevents the growth of bacteria in foods because it decreases their (pH) .It has many industrial uses, and is added to frozen fruits to retain their

colour and taste .

5- **Lactic acid** $CH_3\text{-}\underset{}{\overset{OH}{\overset{|}{C}}}H\text{-}COOH$

It is found in milk as a result of the effect of enzymes secreted by certain kind of bacteria on milk sugar (lactose). It is generated in human body as a result of hard effort, and causes a constriction in muscles .

6- **Ascorbic acid vitamin (c):**

The human body needs vitamin C in small quantities . It is found in citrus fruits, vegetables and green pepper.It decomposes by heat and the effect of air. Lack of vitamin C leads to deterioration of some biological functions in the human body and the infection whith "Escarpot" disease, from its symptoms, bleeding of gum and joints swelling.

7- **Salicylic acid**

It is used in the manufacture of cosmetics specific to skin , because it make it more soft, flexible and protect it against sun rays and in elimination of skin warts and acne. It is also used in preparation of Aspirin.

8- **Amino acids**

Amino acids are known as amino derivatives of organic acids. The simplest member of amino acids is glycine which is known also as amino acetic acid $NH_2\ CH_2\ COOH$. It is formed by replacing one hydrogen atom in the alkyl group of the acid molecule by an amino group ($-NH_2$)

$$\underset{\text{Anino group}}{NH_2} + \underset{\text{Acetic acid}}{H\text{-}CH_2COOH} \rightarrow \underset{\text{Glycine (amino acetic acid)}}{NH_2\text{-}CH_2\text{-}COOH}$$

Amino acids are numerous in nature but only twenty of them are found in natural proteins.

The amino acids which form proteins are of the (α) amino type , i.e. the amino group is attached to the (α) carbon atom which is directly attached to the carboxylic group. Proteins are considered as polymers of amino acids

$$R\text{ - }\underset{NH2}{\underset{|}{\overset{\propto}{C}}}H\text{ - }COOH$$

Evaluation on organic acid

QUESTION 1:-

Which of the following compounds are carboxylic acids.

1- $CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

2- CH_3-CHO

3- $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_3$

4- $HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

5 – $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH$

QUESTION 2:-

Write the structural formula of the compounds which have the following molecular formula :

1. Dicarboxylic aromatic acid $C_8H_6O_4$.
2. Aromatic acid contain a carboxylic group and one hydroxyl group $C_7H_6O_3$
3. Dicarboxylic aliphatic acid $C_2H_2O_4$.
4. Aliphatic ether $C_4H_{10}O$.
5. Three alcohols having the molecular formula $C_4H_{10}O$.

QUESTION 3:-

Write the chemical formula of the following acids:

1) Formic acid
2) Acetic acid
3) Benzoic acid
4) Salicylic acid
5) 2 , 2 - dimethyl butanoic acid.
6) 2 , 3 - dichloro hexadecanoic acid
7) 2 , 4 - dichloro benzoic acid.

QUESTION 4:-

Write the structural formula of the acid produced from the oxidation of the following:

1- CH_3OH 2- CH_3CHO 3- CH_3-CH_2-CH_2-CH_2OH

4- $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \overset{\displaystyle O}{\overset{\|}{C}} - H$

QUESTION 5:-

Write the name of the following compounds then explain how to prepare each one by neutralization process.

1- CH_3COOK 2- $(HCOO)_2Ca$

3- C_6H_5COONa 4- CH_3CH_2COONa

QUESTION 6:-

(a)Formic acid	(c) Ethanoic acid	(e) Oxalic acid
(b)Salicylic acid	(d) Butyric acid	(f)Benzoic acid

From the previous table mention the following :

1- Monocarboxylic acid.

2- Dicarboxylic acid.

3- An acid in which the number of carboxylic groups equals the number of carbon atoms.

4- An acid contains two functional groups.

Esters

Esters are the products of the combination of carboxylic acids with alcohols. This can be represented by the general formula.

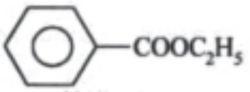
$$\underset{\text{Acid}}{R-\overset{\overset{O}{||}}{C}-OH} + \underset{\text{Alcohol}}{H-OR} \rightleftharpoons \underset{\text{Ester}}{R-\overset{\overset{O}{||}}{C}-OR} + H_2O$$

Esters are widely spreaded in nature. They are present in all plant and animal materials. Most of the ester are characterized by a pleasant smell which is responsible for the odour and flavour of fruits and flowers. Many organic esters have been prepared for the commercial production of perfumes and flavours and are used either alone or mixed with natural compounds. The odour of the ester decreases by the increase of the molecular mass of the alcohol and acid used for their formation .The nature of the ester changes from a liquid with a pleasant odour to a waxy solid which is nearly odourless. Waxes such as bee wax are high molecular mass esters. Fats and oils are ester derived from glycerol which is a trihydric alcohol and high fatty acids.

The name of an ester is derived from the name of the acid radical and the name of the alkyl group of the alcohol as shown by the following examples

$HCOOCH_3$
Methyl formate

$CH_3COOCH_2CH_3$
Ethyl acetate



Ethyl benzoate

The direct method for the preparation of esters , is the reaction between the carboxylic acid and the alcohol . For example the ethyl acetate is obtained by the reaction of acetic acid and the ethyl alcohol.

$$\underset{\text{Acetic acid}}{CH_3COOH_{(l)}} + \underset{\text{ethanol}}{C_2H_5OH_{(l)}} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_{5(aq)}} + H_2O_{(l)}$$

This reaction is reversible where the formed ester is hydrolyzed to the acid and alcohol. It is preferred to use a dehydrating agent such as concentrated sulphuric acid or hydrogen chloride gas to get rid of the formed water

Physical properties:

Most of the esters are liquids with much lower boiling point than those of the acids or alcohols of nearly equal mass .This is due to the absence of the polar hydroxyl group which is found in alcohols and acids and leads to the association of molecules of each of them with hydrogen bonds.

		The acid	Alcohol	Ester
The molecular weight = 60 g/mol		Acetic acid CH_3COOH	propanol C_3H_7OH	Methyl formate $HCOOCH_3$
	Boiling point	118°C	97.8 °C	31.8 °C
The molecular weight = 74 g/mol		C_3H_7COOH Propanoic acid	C_4H_9OH butanol	CH_3COOCH_3 Methyl acetate
	Boiling point	141 °C	118 °C	57 °C

Chemical properties :

1- **Hydrolysis** Alcohol and acid are produced from the hydrolysis of ester i.e. reverse to ester formation reaction.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + H_2O \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R\,OH$$

a- Hydrolysis may take place by the use of dilute mineral acids as a catalyst and is called (acid hydrolysis).

$$H_3C\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OC_2H_{5\,(l)} + H_2O_{(l)} \xrightarrow{H^+} CH_3COOH_{(aq)} + C_2H_5OH_{(l)}$$

b- Hydrolysis of esters may also be carried out by heating with aqueous alkalis, to produce the alcohol and the salt of the acid. This is called alkaline-

hydrolysis or saponification (Since soap is the sodium salt of high carboxylic acids).

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5}_{(l)} + NaOH_{(aq)} \rightarrow \underset{\text{sodium acetate}}{CH_3COONa}_{(aq)} + C_2H_5OH_{(l)}$$

$$\underset{\text{ethyl benzoate}}{C_6H_5COOC_2H_5}_{(l)} + NaOH_{(aq)} \rightarrow \underset{\text{sodium benzoate}}{C_6H_5COONa}_{(aq)} + C_2H_5OH_{(l)}$$

2- <u>Ammonolysis :</u>

Esters react with ammonia to give acid amide and the alcohol.

$$\underset{\text{ethyl acetate}(l)}{H_3C\text{-}\overset{\overset{O}{\|}}{C}\text{-}OC_2H_5} + NH_{3(g)} \longrightarrow \underset{\text{acetamide}(l)}{CH_3-\overset{\overset{O}{\|}}{C}\text{-}NH_2} + C_2H_5OH_{(l)}$$

$$\underset{\text{ethyl bezoate}(l)}{C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}OC_2H_5} + NH_{3(g)} \longrightarrow \underset{\text{benzamide}\ (l)}{C_6H_5-\overset{\overset{O}{\|}}{C}\text{-}NH_2} + C_2H_5OH_{(l)}$$

The important uses of esters in our life may be clearified in the following:

1- <u>Esters as flavour</u>

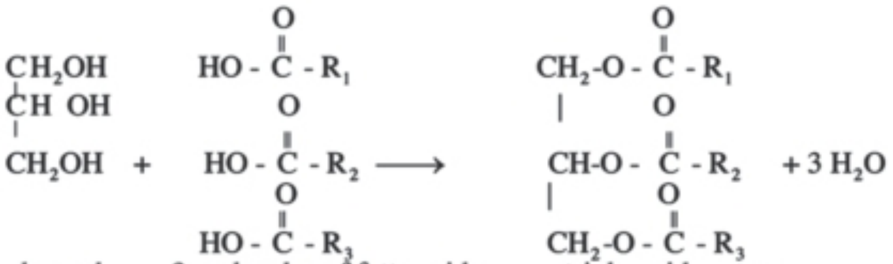
Ester are characterized by pleasant smells and tastes .That is why they are used in food industries as flavours .

The following table shows the common uses of some esters (for reading only).

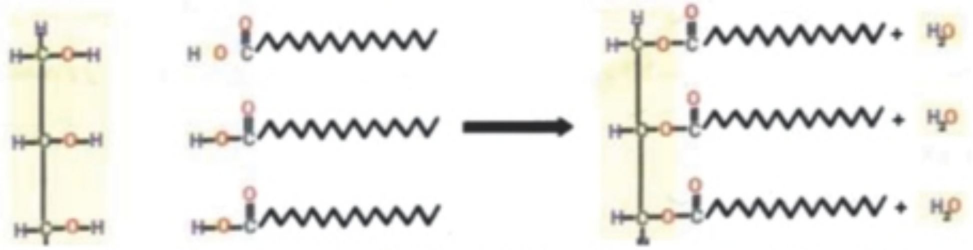
Ester	Chemical formula	The odour
Isobutyl formate	$H-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{CH_3}{\mid}}{CH}-CH_3$	Cherries
Propyl acetate	$CH_3-\overset{\overset{O}{\|}}{C}-O-C_3H_7$	Pear
Benzyl formate	$H-\overset{\overset{O}{\|}}{C}-O-CH_2-C_6H_5$	Apricote
Methyl butanoate	$CH_3-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-CH_3$	Pin apple
Propyl formate	$H-\overset{\overset{O}{\|}}{C}-O-C_3H_7$	apple
Pentyl acetate	$CH_3-\overset{\overset{O}{\|}}{C}-O-C_5H_{11}$	banana

2- Esters as Fats and oils:

Fats and oils are esters produced from the reaction between organic acids and glycerol. Their molecules are called **triglyceride** because each molecule is formed from the reaction of one molecule of glycerol (trihydric alcohol) and three molecules of fatty acids. The acid molecules may be similar or different, saturated or unsaturated with long or short chain.



glycerol   3 molecules of fatty acids   triglyceride ester



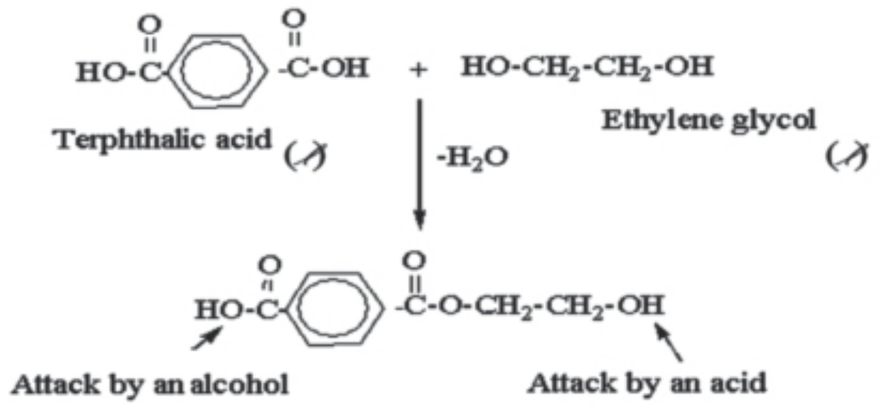
Glycerol   three molecules of different fatty acids   ester triglyceride   water

N.B : Hydrolysis of fat or oil (ester triglyceride) in the presence of strong alkali like (NaOH) or (KOH) is known as **saponification** process which is the principle reaction in the manufacture of soap and glycerol.

3- Esters as polymers (Poly ester):

Polyesters are polymers produced from the condensation of two monomers one of them is a dibasic acid and the other one is a dihydric alcohol.

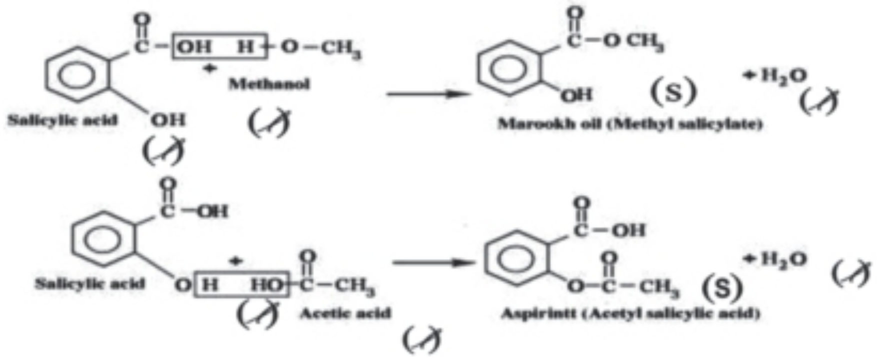
The most common poly ester is **Dacron** fibers which are prepared by the reaction between terphthalic acid and ethylene glycol (ester formation reaction).



The condensation process proceeds continuously where the alcohol end of the ester reacts with the carboxylic group of a new acid molecule or the acid end of the molecule may be attacked by a new alcohol molecule. By the repetition of the condensation process a very long molecule which is called poly ester is formed. Since Dacron is inert it is used to substitute the spoiled arteries and in the manufacture of artificial heart valves.

4- Esters as medical drugs :

Organic esters are used in the manufacture of many drugs, the most common and simplest one is **aspirin** and oil of winter green (**Marookh oil**) which is used as local oil absorbed by the skin to decrease the pains of rheumatism. The acid which is used in the manufacture of these two drugs is **salicylic** acid. Its molecule contains both the carboxylic and hydroxyl groups. It reacts as an acid or as an alcohol as following equations.

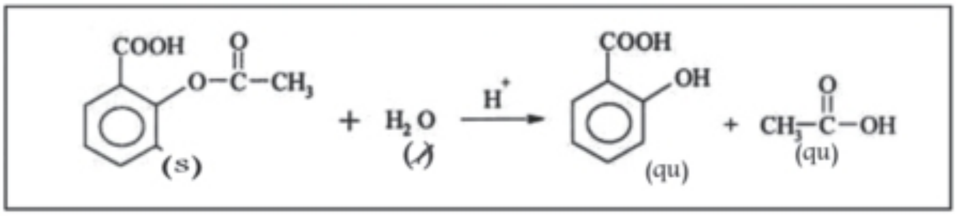


Aspirin

Aspirin is the important drug which reduces the headache pains and temperature It also reduces the blood clotting and prevents the heart crises.

The active substance in aspirin is salicylic acid however, the addition of **acetyl group** to the acid decreases its acidity effect and becomes tasteless.

Aspirin is hydrolysis in the body to produce salicylic acid and acetic acid.



The produced acids causes the excitation of stomach walls, and may cause stomach ulcer. Therefore doctors advice to crush the aspirin tablet as a powder before swallowing or taking it dissolved in water. There is a type of aspirin mixed with an alkaline substance like. aluminum hydroxide to neutralize the acidity produced.

Ester Evaluation

QUESTION 1:-

(a) Aspirin	(c) $(COO)_2Ca$	(e) $C_6H_5COOCH_3$
(b) $CH_3COOC_6H_5$	(d) Vitamin C	(f) Dacron

From the previous table define the following :

1- The esters.
2- The carboxylic acids.
3- The ester produced from the reaction of benzoic acid and methanol.
4- Two isomeric compounds.

QUESTION 2:-

Explain why the solubility of the ester in water is less than the solubility of the Corresponding acid which contain the same number of carbon atom?

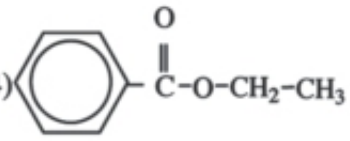
QUESTION 3:-

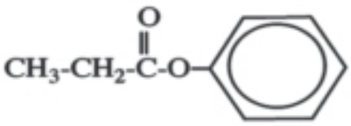
Write the common and IUPAC names of the following esters :

1) $CH_3-CH_2-\overset{O}{\overset{\parallel}{C}}-O-CH_3$

2) $H-\overset{O}{\overset{\parallel}{C}}-O-CH_3$

3) $CH_3-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-O-CH_3$

4) 

5) 

QUESTION 4:-

(a) Methyl acetate	(c) Sodium acetate	(e) Ethanoic acid
(b) Methyl formate	(d) Potassium acetate	(f) Ethyl formate

From the previous table illustrate the following :

1- The esters 2- The salts of the carboxylic acids.
3- The isomeric compounds.
4- The compounds which take a name according to IUPAC system.

QUESTION 5:-

(a) $CH_3 - \overset{\overset{\large O}{\|}}{C} - O - CH_3$	(c) $CH_3 - \overset{\overset{\large O}{\|}}{C} - O^- Na^+$	(e) CH_3CH_2COOH
(b) $CH_3 - \overset{\overset{\large O}{\|}}{C} - CH_3$	(d) $CH_3 - \overset{\overset{\large O}{\|}}{C} - OH$	(f) $CH_3 - \overset{\overset{\large O}{\|}}{C} - O - C_2H_5$

From the previous table define the following :

1- Compounds when hydrolyzed produce ethanoic acid.

2- Compounds used in their preparation ethanoic acid.

3- Compounds react with caustic soda, solution

4- Compounds give effervescence when react with sodium bicarbonate.

QUESTION 6:-

Write the chemical name of each of the following:

1- Aspirin	2- Fats and oils	3- Teflon
4- Vitamin C	5 TNT.-	6- PVC.